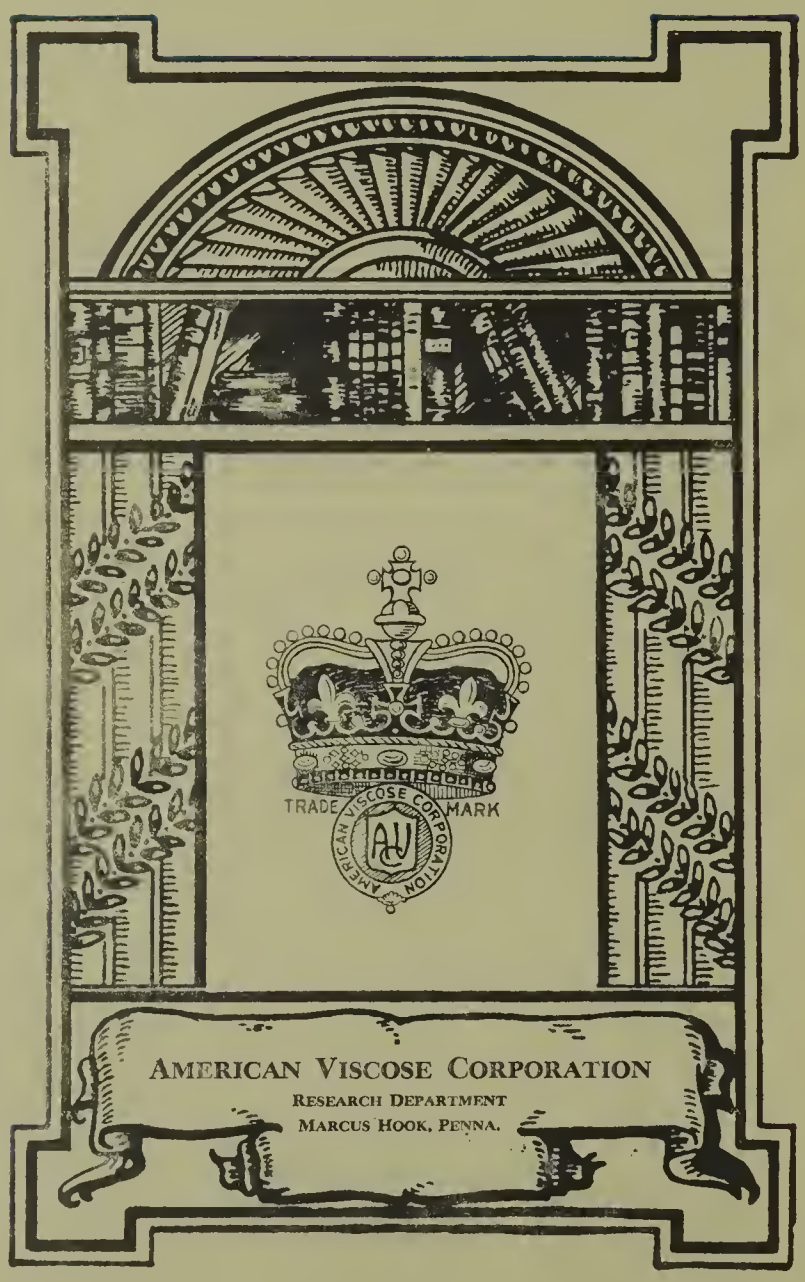
Edward Barton.



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TRANSACTIONS

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TRANSACTIONS OF THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

EARLY COMMERCIAL ELECTROLYTIC CELLS

By CHARLES B. BARTON

Read at Montreal Meeting, June 28, 1920

The paths of the early workers on electrolytic cells were not strewn with roses. They were very rocky. I speak from experience for I think I have been continuously in the business longer than any other man in this country. In September, 1894, I went to work for the old Electrochemical Company of Rumford Falls, Maine, as a laborer, 20 months later I was made superintendent of the plant, and have held that position there, and subsequently in Berlin for the Brown Company. That makes 26 years of experience.

The original cells in Rumford Falls were the old belljars, with an asbestos diaphragm, approximately horizontal. The anodes were of retort carbon and were cast in lead, a projecting portion coming through the top of the belljar, to which was connected the positive wire. The cells were supposed to take about 100 amperes each and were run in parallel in the iron tanks, the tanks being connected in series. The diaphragms of these cells had to be changed very often, the units were too small, and when I entered the employ of the company, they had discarded this type and were changing the type of cell.

These second cells were square boxes about 24×24×24 inches, the top and upper third of the outside being made of slate with a slate cover, a wooden leg on each corner and a wooden bottom. Around the open part asbestos paper was wound and outside of this wire netting, the netting being turned on the bottom of the cell, so as to give electrical contact with the bottom of the iron tank, which held the cathode bath. The anodes were of gas carbon, with the ends cast in lead and space between the central anode proper and the

asbestos diaphragm was filled with lumps of broken retort carbon, the object being twofold: to hold the diaphragm against the cathode and to bring the active anode surface closer to the cathode surface. About 500 of this type cells were discarded and another type later installed.

The third type of cell was a slate box with gas retort carbon anodes and no packing between the anode and diaphragms. They were of various sizes, a large number of about 36 inches in length by 6 inches wide and about 18 inches deep. These cells are very similar in construction to cells in commercial operation to-day. They were, however, soon discarded in favor of another type installed.

The fourth type was a distinct departure from the previous types. It was a large unit and was contained in a cathode tank, 9 feet long, 5 feet wide and 18 inches deep. A wooden frame of 4×6 inches lumber was laid in the bottom of the tank, on this frame a grid of iron made of $\frac{3}{8} \times 1\frac{1}{2}$-inch iron was laid and part of the irons were extended and bolted to the tank to make contact with it. These irons were inclined to the horizontal so there was a pitch of 2 inches to the foot. On top of these irons, a wire netting was placed to act as the cathode proper, and on top of this cathode a diaphragm of asbestos paper was laid. The side walls of the cells were made of red brick and the diaphragm was cemented in with quick hardening cement. The covers were slate and the anodes were platinum wire. About fifty of these were operated during the spring and summer of 1898. The design was good and with the substitution of perforated metal plate for the iron grid and concrete side walls for the brick and wood the same cells are running to-day and efficiently.

The plant of the Electro-Chemical Company of Rumford Falls closed in the fall of 1898, and part of the plant and operating personnel were transferred to Berlin, New Hampshire, to make chlorine for bleaching the pulp of the Burgess Sulphite Fiber Company. Mr. T. P. Burgess, the manager of this plant, believed in the future of electrolytic chlorine and he believed that experience was the most valuable asset he could buy. He bought the experience of the Rumford Falls plant and he paid a very low price for it. The stockholders of the Electro-Chemical Company shouldered their loss. The stockholders of American electrolytic chlorine and caustic soda corporations owe to stockholders of the old Electro-Chemical Company at least a debt of gratitude. Let us analyze the reasons why the different cells developed at the Rumford Falls plant were not a success

commercially. The first cells of the old belljar type failed because they were too small a unit, the diaphragms broke too often, and they were connected in parallel in the cathode tanks. The second cells failed because of the wooden construction of the body, the fact that the anode compartment was filled with broken pieces of carbon so as to give very poor circulation, and because of the method of making electrical contact to the anodes which, you will recall, was by casting the upper ends in lead. The lead soon became oxidized at the points of contact and this caused a rising voltage and uneven distribution of current in the tanks for these cells had the fault of the previous ones, that they were connected in parallel.

The third type of cells failed because the same method of making electrical contact with the anode, casting in lead was used, because the cells were connected in parallel, because too small a chlorine chamber was left in the cell and because the material of which they were composed, slate, was not the proper material of which to make cell bodies.

The final type of cell developed at Rumford Falls was a commercial failure there, because the stockholders did not care to sink any more money in the plant. It was a success in Berlin.

I think it is proper at this time to state that Mr. E. A. LeSueur had no active part in the management of the Rumford Falls Electro-Chemical Company until the original development funds were about all spent. After the original management had demonstrated they could not run the plant at a profit, he was made manager but, there was so little money available for experiments, and development that the plant could not be developed to a commercial success. The offer from the Burgess Sulphite Fiber Co. to take over the plant came while the plant in Rumford was still in operation and was accepted as an easy way out of an exceedingly uncomfortable financial condition.

It is now time to mention a few of the difficulties of operation encountered in the infant industry. The draft for moving the chlorine was originally obtained by introducing a pipe into the draft tube of the water wheels. It was later produced by steam syphon. The gas pipes to all the first cells were of lead and of small diameter, so that they were always clogging up. The brine was fed to the cells by means of a dipper and a funnel through a hole in the top of the cells, and when acidulated brine was introduced to a cell whose anode compartment was full of sodium hypochlorite, the foam imme-

diately clogged the gas pipes and imparted a green tint to the atmosphere. In fact, the atmosphere of the cell houses was usually slightly green and all men who entered the cell houses wore muzzles. A cell whose anode compartment was contaminated with alkali always runs at a low current efficiency. The oxygen liberated at the anode immediately attacked the amorphous carbon and formed CO_2 with which the chlorine was contaminated. The lime spread in the bleach chambers absorbed the CO_2 and this lowered the test of the bleach so that it was not always salable, in competition with English bleach. It was observed, however, that the CO_2 always combined with the top lime and formed a hard crust. It was necessary to skim off this top crust in order to produce merchantable bleach. This difficulty finally led to experiments with platinum anodes. Platinum anodes seemed to promise elimination of our troubles. It was necessary because of financial reasons to use the smallest amount of platinum possible. Mr. LeSueur produced a platinum anode which was based on the idea of the electric light bulb. Sixteen pieces of platinum wire about 4 inches long were sealed in a glass tube in the same manner, as was formerly usual in making light bulbs. About $\frac{1}{4}$ inch of wire was left inside the tubes, and the outside wires, which were flattened, were spread like the spokes of a wheel at right angles to the tube. Electrical contact to the inside wires was made by a drop of mercury. It was necessary to have a horizontal diaphragm to use this anode, and they were used in the last type of cell installed in Rumford Falls.

The money for this last installation was very meager. The directors wanted a profit or they wanted to close down the plant, and not enough platinum anodes were allotted to each cell to safely carry the load. The result was that many of them cracked. This threw the load on the remainder with the result that the cells ran at very high voltages, which ran from 5.5 to 7.5 or 8 per cell, at 1200 amperes with about 30 square feet of diaphragm per cell. This produced a very peculiar and puzzling result. The temperature rise was so great that sodium chlorate was formed in large amounts; the caustic liquor going to the kettles contained only about 2% NaCl, but the finished product would contain about 10%. When the reason was discovered all caustic liquor was treated with potassium chloride, we were obliged to go into the manufacture of chlorate of potash. It was at the time of the Spanish-American War and chlorate of potash, being contraband, shot up in price, so that it

really was a blessing in disguise, and allowed us to weather the gale for a little longer. However, after the offer from the Burgess Sulphite Fiber Co., we soon shut down and thus closed the first commercial American plant of porous diaphragm cells for the production of chlorine and caustic soda.

McDonald and Mercer were foremen of the cell houses in Rumford Falls. H. K. Moore had his first experience with cells in the employ of the Rumford Falls plant. The Nelson cell was born of experience with the McDonald cell, which was a copy of the third type of LeSueur cell. I should like to read some claims of the LeSueur cell patents granted in 1891, now lapsed.

> "An electrolytic cell comprising a bell of earthenware, a positive electrode therein, a diaphragm covering the mouth of said bell, a negative electrode, and a tank in which said bell is placed, the level of the liquid within the bell being higher than that of the liquid outside the bell, whereby the diaphragm is prevented from bulging, substantially set forth.
>
> "3. An electrolytic cell comprising a combination, with a tank to contain liquid, of a bell in said tank, positive and negative electrode, and a flexible diaphragm between said electrodes and covering the bottom of said bell, said diaphragm being adapted to maintain the liquid of the positive electrode side of the said diaphragm on a higher level than that of the liquid of the negative side of the diaphragm, whereby the diaphragm is kept from approaching the positive electrode, substantially as set forth."

In the LeSueur electrolytic patents, the principle of having on the anode side of the diaphragm a greater hydrostatic head than is carried on the cathode side is first mentioned.

Unless I am greatly mistaken, these patents were the foundation of all electrolytic porous diaphragm cells, and credit should be given E. A. LeSueur as being the real founder of the industry. When we moved to Berlin, New Hampshire, in October, 1898, it was with the purpose of making bleach liquor for bleaching the pulp, and letting the caustic run to waste. The plant was a success from the start, though handicapped in various ways. Seventy-two cells were installed to run at about 1000 amperes. The writer should have known better from past experience, for he made a mistake in starting the original plant in using the exhaust steam from the engine that

furnished the auxiliary power to heat the water that was run in the cathode compartment to flush out the cathode liquor. This made the cathode liquor so active that it diffused into the anode compartment to such an extent that it seriously effected the efficiency of the plant. This mistake, was, however, soon rectified, and the trouble eliminated. The power for the operation of the cells in Berlin was bought under a peculiar arrangement. The power from four water wheels, a maximum of about 1000 H-P. was contracted for at a low figure, when there was water enough in the river to run these wheels. The other six wheels in the same power house having prior right to the water and running the saw mill. The result was that the power was very uneven and in the winter of 1899–1900 it was necessary to shut down the cells and close up the plant for lack of power. The writer moved to the sulphite mill and set up some experimental cells in the digester building. There we ran experiments for several months, mostly on cells of the Moore type, and with the new Acheson graphite, which had just them come on the market. In plotting the variables, and trying to find why some cells ran better than others, I found that by manipulating the flow through the diaphragm in proportion to the amperes going through the cells, using saturated brine, I could get any results I desired within certain limits. If you wanted to get 97 or 98% current efficiency, we simply increased the flow to the point necessary. This would decompose about 50% of the salt in the brine fed to the cell. If you wanted to decompose about 60% of the salt we reduced the flow to the point on the curves that would give this figure, and would get about 90–91% current efficiency. It was very simple. As Mr. Burgess said, we seemed to have the world " by the tail," and all we needed to do was to swing it.

We immediately designed a cell and installed 160 of them, the original Moore cells, the first cells run commercially with submerged cathodes. There were mistakes made in the construction. The frames were made of slate put together with wood screws. They were installed in a single row, on about 8-inch centers. The graphite was not impregnated, the brine was not purified. The gas outlets were 1-inch glass tubes. The gas space in the cells was too small and they vomited chlorine continuously. We lived, I don't know how, with them nine months, and then threw them all out the back windows, and called it good riddance. The principle was all right but we did not work it out to its logical conclusion. I had been steeped in chlorine for nine months and cared nothing about principles or

conclusions. Now, however, we had Acheson graphite. The graphite from the Moore cells was used in the LeSueur cells and we soon began to get wonderful results for that time. The voltage drop on individual cells was 4 to 5 volts, instead of 5.5 to 6.5 with a platinum anode. The production jumped, while the power required per ton of bleach was lowered from 100 to 125 E.H-P. to 80–90 and, of course, in later years to 60–70. The real future of the Electrolytic cell dawned with Acheson graphite anodes. The original plant in Berlin had grown from 72 cells, with a production of 3–6 tons of bleach per day, to a plant with about 800 cells and a maximum production of 80–90 tons 35% bleach. The water wheels that formerly furnished power for the saw mill and caused the shutting down of the bleach plant wheels are now furnishing power for the cells as well as all the other wheels in the next lower power house, and half the wheels on the one below that. We have installed 160 of the latest type of Allen-Moore calls which resemble the original ones only in principle. Mr. H. I. Allen developed the cell from the point we left it.

About the same time the LeSueur cells were started in Berlin, New Hampshire, in 1898, an installation of Carmichael cells was started at the Westbrook, Me., plant of the S. D. Warren Paper Company. These cells used platinum wire anodes and the gravity principle of separation. They were not a commercial success.

The history of the development of the diaphragm electrolytic cell emphasizes the well-known point that new processes are best developed by well-organized corporations, engaged primarily in some other business that can bear the financial burden of experimental failures and keep on until success crowns their efforts.

DISCUSSION

President Wesson: We owe many thanks to Mr. Barton for his able exposition of the subject of Commercial Electrolytic Cells. I can sympathize with some of the troubles he had in those days because I ran some cells of somewhat the same style but they never became commercial. I did not invent those cells but they were brought into the company by a man named Cutten whose name appeared in the patent literature, and about which I do not care to say much. The paper is now open for discussion.

Mr. Max Mauran: I would like to make addition to Mr. Barton's paper. I think he made the statement that the efficiency of the cells was greatly increased by the use of Acheson Graphite anodes, and that the cells in question were the first in which graphitized carbons were used. I do not wish to depreciate the wonderful work or discredit in any manner Dr. Acheson, but the first graphitized carbons used in the electrolytic cell, for the decomposition of sodium chloride, were those manufactured for the Castner process after graphitizing methods invented by Hamilton Y. Castner, and it is for the purpose of perpetuating his name in history that I mention this fact.

President Wesson: But those were not of American graphite.

Mr. Mauran: Castner cells were first operated in the United States during the latter part of 1895 and January, 1896. These cells were equipped with graphitized carbons which were graphitized in America. I assisted with the design of furnace for graphitizing carbons as long ago as the winter of 1895–1896, and when I came to Niagara in the winter of 1896–1897 I saw in operation a furnace built for the production of carborundum. It occurred to me that this type of furnace, with some slight modification, could be used for the graphitizing of electrodes to be used in the Castner cells that were being installed at the plant of the Mathieson Alkali Works at Niagara at that time. Arrangements were made with the Carborundum Company, I don't remember the exact date, to graphitize carbons for the Mathieson Alkali Works, and a number of tons of carbons were graphitized by them during the year 1906–1907. It was some years later, if I remember correctly, that the International Acheson Graphite Company was formed.

Mr. Hugh K. Moore: In relation to the last speaker, I will say

I am glad to have this information as to who made the first graphitized carbon. Graphitized carbon then was a curiosity rather than an actuality. It was not made commercially in large quantities. In 1897 one of my classmates working at Niagara sent me one of the first small pieces of graphite which was made electrically, and I think I was the first person who ever used graphite carbon in electrolytic cells.

Mr. LeSueur: There are many things which might be touched on in connection with this industry which can be imagined when you consider the entire lack, thirty years ago, of the rugged appurtenances which now exist, a sufficient number of which were developed by me so that we were able during the nineties at Rumford Falls to take the business out of the test-tube scale and ship our product in box cars, tank cars and flat cars. I remember, when I started to work in the eighties that one Hempel did some work in a glass tube with 0.4 ampere which attracted attention, so that the 200-ampere electrolyzers with which we started were very large indced.

We made a great many million pounds of bleach and alkali. Mr. Barton has read certain claims of one of my first patents issued April 7, 1891. While still in college I was put into the hands of a firm of patent attorneys who were highly recommended, and I believe they were excellent men in boot and shoe machinery, but what they did not grasp about the essential electrochemical points was considerable; but the blame was mine for not realizing that they did not grasp it. What they did not accentuate was the fact, set forth in the specifications but not properly claimed, namely that it was most desirable that there should be an excess of pressure on the anode side of the diaphragm. That, as I discovered in the early nineties, was only half of it, and the other half was that you must use a diaphragm which is mechanically, not merely molecularly, porous. Take a thing like a bladder or membrane, which allows diffusion but does not allow the physical flow which is essential,—in spite of any head which could practicably be put on it the alkali would work right back into the anode compartment. I discovered the essential method of working, which was to establish such an excess head on the anode side of the diaphragm so that the amount of physical flow of anodic solution, due to such excess head, would wash back into the cathode compartment the alkali which would otherwise diffuse, in spite of such excess head, away from said compartment.

Mr. Barton later formulated the beautiful law showing the definite relation between the amount of physical flow of the electrolyte into the cathode compartment and the chloride decomposition efficiency, and not only formulated it but prescribed its limits. (Applause.)

Mr. Barton: We did some awfully foolish things then. We had no appliances; little money; we were only twenty-two or twenty-three years old, but we did accomplish something, and I take pride in the fact that I think we laid the foundations of the industry. Other people went ahead and took out better patents than we did, and no doubt they made better cells than we did, but if you investigate, you will find that all the development started right there at Rumford Falls where we breathed chlorine and lived with it for some time. (Applause.)

President Wesson: We have certainly been interested in this discussion.

THE FUNDAMENTALS OF ELECTROLYTIC DIAPHRAGM CELL

By HUGH KELSEA MOORE

Read at Montreal Meeting, June 28, 1920

In 1897 E. A. Allen and H. K. Moore introduced a cell in which was claimed the basic principle of having the cathode unsubmerged in the electrolyte. During the twenty-three years which have elapsed since this time this principle has revolutionized the entire cell industry in the United States.

The first experimental cells built had horizontal diaphragms submerged in a bath of kerosene oil and the caustic as it was formed on the cathode sank to the bottom of the oil and was siphoned off from the bottom. On account of danger of fire, experiments on this line were discontinued and the experiments were conducted having the cathode unsubmerged in the electrolyte but with no oil to balance the static head of the liquor in the anode compartment. Owing to the importance which the unsubmerged diaphragm cell has assumed in the electrolytic industry, it might be well to discuss the fundamental principles involved.

In order that there may be no misunderstanding in regard to the unsubmerged diaphragm cell, I wish to mention that one type of cell represented by the Hargreaves-Bird cell, used for the production of carbonate of soda and chlorine, had an unsubmerged cathode. This type of cell, however, was not available for the production of caustic soda and so far as I know has never been capable of producing caustic soda. In this cell the diaphragm was so impregnated as to prevent the percolation of the electrolyte. The unsubmerged diaphragm type of cells to which I refer allows the electrolyte to percolate through the diaphragm.

Suppose we start with the fundamentals. If a compartment filled with salt brine is divided into two parts by a permeable diaphragm and an anode inserted in one compartment and a cathode in the other and a direct current passed there through, we have chlorine

liberated at the anode and casutic soda liberated at the cathode according to the following equation.

$$NaCl + H_2O = \overset{+}{Cl} + \overset{-}{NaOH} + \overset{-}{H}.$$

If the passage of the current is continued we obtain an electrolyte constantly decreasing in percentage of salt and constantly increasing in percentage of caustic soda. There will also be a slight increase in the percentage of water in spite of the fact that water is used up in the production of caustic soda. This is due to loss of chlorine which overbalances the loss of water. (See Table I and Chart I.)

TABLE I

PRODUCTS RESULTING FROM ELECTROLYTIC DECOMPOSITION OF 26% BRINE SOLUTION

Begin with 100 gms. of 26% Brine Solution

Per Ct. Decomposition	Grams H_2O Remaining.	Grams NaCl Remaining.	Grams NaOH Produced	Grams Cl_2 Evolved.	Grams H_2 Evolved.	Resulting Solution.		
						Per Cent NaCl.	Per Cent NaOH.	Per Cent H_2O.
0	74	26.0	0	0	0	26.00	00	74.00
5	73.6	24.7	.89	.79	.02	24.90	.90	74.20
10	73.2	23.4	1.78	1.58	.04	23.79	1.81	74.40
15	72.8	22.1	2.67	2.37	.07	22.66	2.83	74.51
20	72.4	20.8	3.56	3.16	.09	21.50	3.68	74.82
25	72.0	19.5	4.44	3.94	.11	20.32	4.64	75.04
30	71.60	18.2	5.33	4.73	.13	19.13	5.60	75.27
35	71.2	16.9	6.22	5.52	.16	17.92	6.59	75.49
40	70.8	15.6	7.12	6.31	.18	16.68	7.62	75.70
45	70.4	14.3	8.00	7.10	.20	15.45	8.62	75.95
50	70.0	13.0	8.88	7.89	.22	14.15	9.66	76.19
55	69.6	11.7	9.78	8.68	.25	12.84	10.74	76.42
60	69.2	10.4	10.67	9.47	.27	11.51	11.84	76.65
65	68.8	9.1	11.55	10.25	.29	10.17	12.90	76.95
70	68.4	7.8	12.44	11.04	.31	8.80	14.02	77.18
75	68.0	6.5	13.33	11.83	.33	7.40	15.17	77.43
80	67.6	5.2	14.22	12.62	.36	5.98	16.35	77.67
85	67.2	3.9	15.11	13.41	.38	4.52	17.54	77.94
90	66.8	2.6	16.00	14.20	.40	3.05	18.74	78.21
95	66.4	1.3	16.89	14.99	.42	1.54	20.08	78.48
100	66.0	0	17.78	15.78	.44	0	21.23	78.77

In this chart it will be noticed that I have used the term "Decomposition Efficiency." To prevent any misconception of the terms hereinafter used I shall at appropriate times give the definition of the terms as I use them and this article should be read and criticised in accordance with the definitions herein given and not by any definition which the reader may have previously used.

A given number of amperes will theoretically produce a given amount of caustic soda in a given time. (See Appendix.) The amount of caustic actually formed, divided by that which should be theoretically formed is therefore the current efficiency. For example, 303 amperes will produce 1 pound of caustic per hour. Consequently if we have 1212 amperes running through a brine solution for one hour and actually obtain 3 pounds of caustic soda, we have $3 \div \frac{1212}{303} = 75\%$ current efficiency.

Decomposition efficiency is the percentage of the salt actually decomposed. Suppose a given sample of caustic effluent takes 6 cc. of $\frac{N}{10}$ H_2SO_4 and 4 cc. of $\frac{N}{10}$ $AgNO_3$, we have $6 \div (6+4) = 60\%$ Decomposition Efficiency. There is a certain theoretical voltage required for the electrolyzer of every electrolyte and any excess of voltage above the theoretical voltage means lost power. For example, we may consider the electromotive force required to electrolyze salt and water into caustic soda, chlorine and hydrogen as 2.3 volts. (See Appendix.)

Now if a cell runs at a current efficiency of 75% with a voltage of 4.1 we have an energy efficiency of $\frac{2.3}{4.1} \times 75 = 42.7\%$ energy efficiency or power efficiency. That is, the energy efficiency is obtained by dividing the theoretical energy required to produce a certain amount of product by the energy actually required to produce that amount of product. Or in other words, the energy efficiency is the percentage of power actually used which is represented by production.

The commercial cell plant endeavors to use a saturated brine for reasons hereinafter explained. Complete saturation, however, is rarely reached but it is practical to obtain a brine of 99% saturation or a brine containing approximately 26% salt.

Table I, illustrated graphically by Fig. 1, shows the varying percentages of caustic soda, salt and water resulting from the electrolytic decomposition of a brine solution containing 26% salt.

These figures are theoretical, for they make no allowance for the small amounts of water evaporated according to the energy efficiency of the cell, for it will be readily seen that the less the energy efficiency of the cell the greater is the amount of heat generated in the cell and consequently the greater the amount of evaporation, provided of course that this is not compensated for by external cooling. The abscissæ show the per cent decomposition efficiencies and the ordinates the varying composition percentages of salt, caustic soda and water.

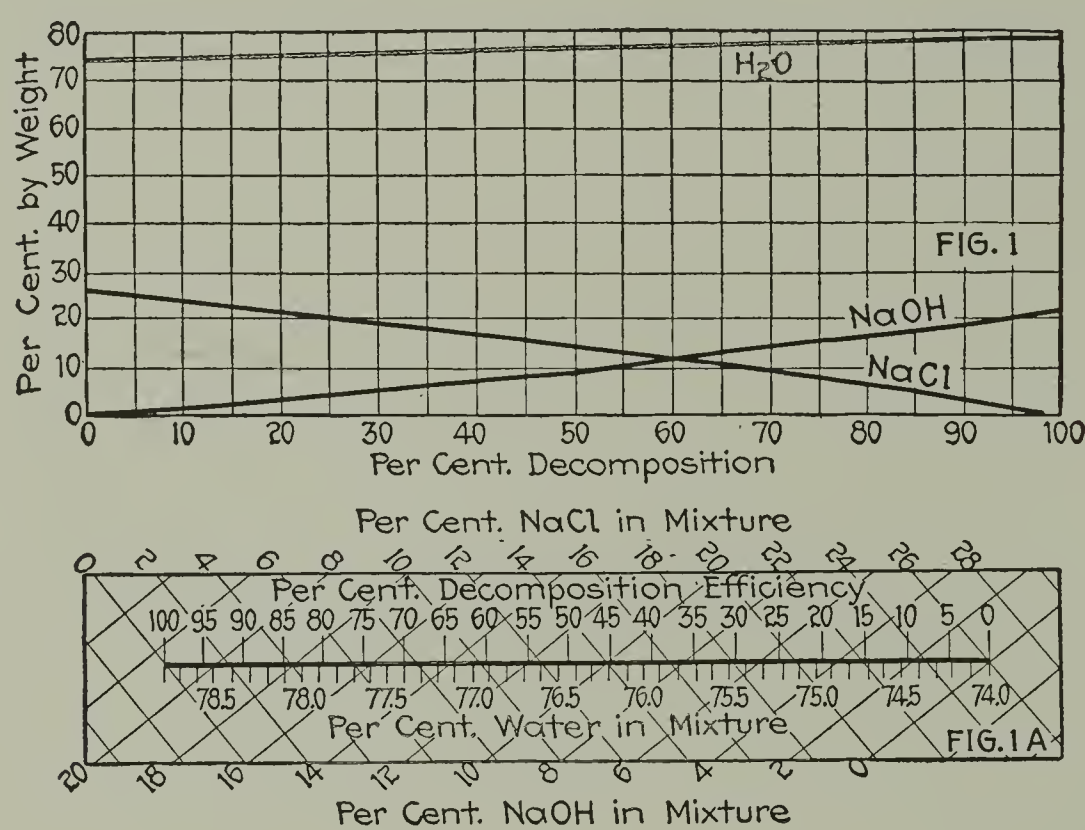


Fig. 1*a* shows this in a different manner on a 3 coordinate chart, all values lying on the straight line A–B. Fig. 1*b* shows the weights in grams of different chemicals, present or formed, in terms of decomposition efficiencies, obtained by electrolyzing 100 grams of a 26% salt solution. Now as the caustic soda increases in strength there is a tendency for this to diffuse by osmotic pressure into the anode compartment.

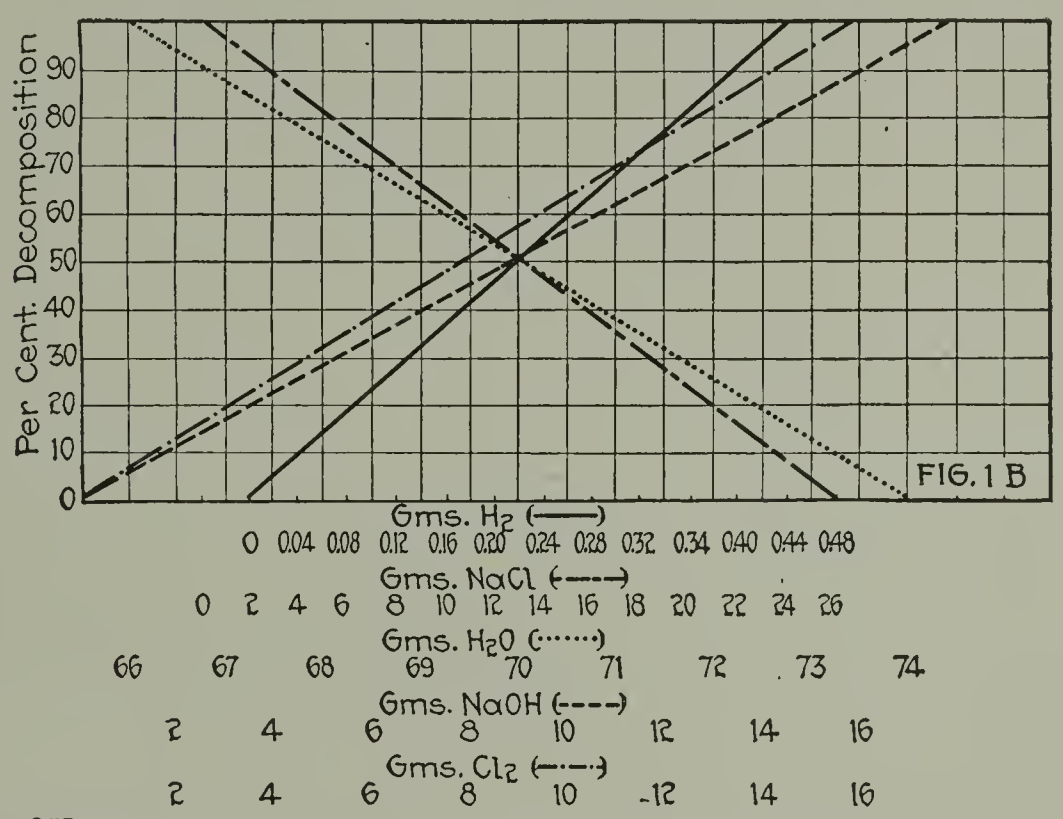
In Table II, illustrated graphically by Fig. 2, will be seen the pounds of caustic which will diffuse through a square foot of diaphragm in an hour with a 26% salt solution from a brine containing different percentages of caustic soda and salt according to the decomposition efficiencies on Fig. 1.

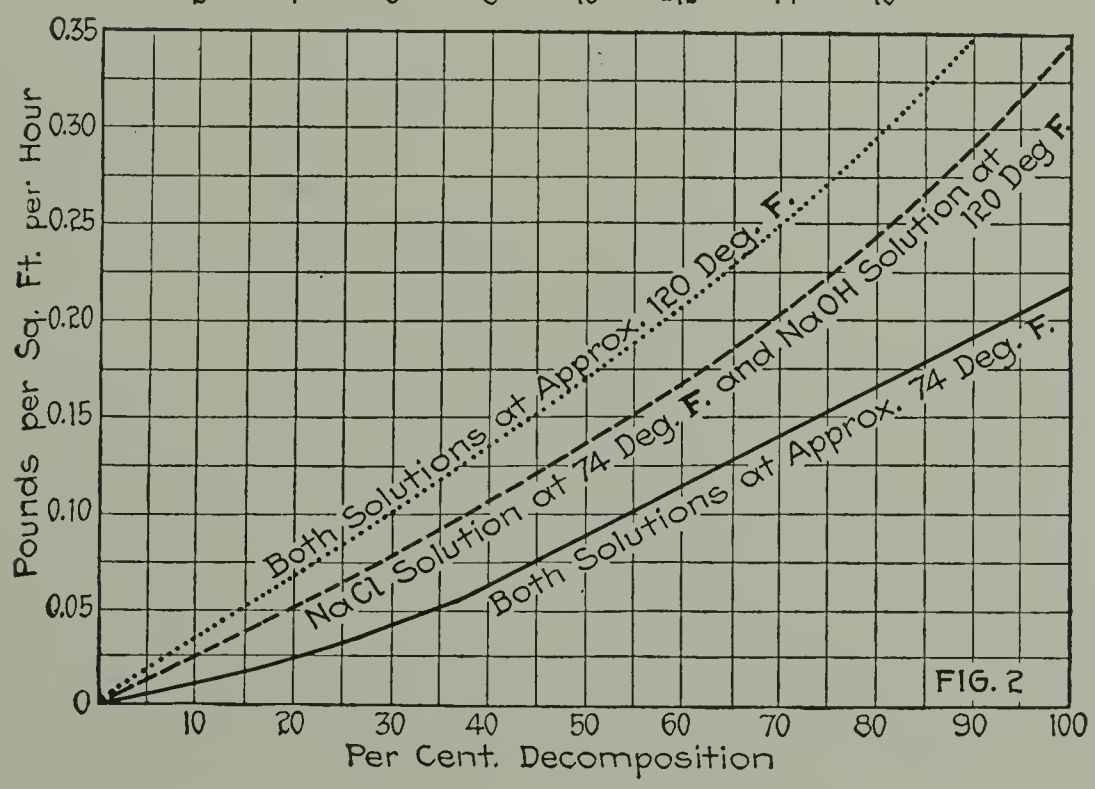
The solid line shows the pounds of caustic per square foot of diaphragm which will diffuse from cold solution of salt and caustic according to decomposition efficiencies (see Table I) into a 26% brine

TABLE II

Pounds NaOH Diffused per Square Foot of Diaphragm per Hour, into 26% NaCl at Varying Decomposition Efficiencies, Temperature of Both 74°

Per Cent Decomp. Eff..	5	10	15	20	25	30	35	41	50	60	70	75	85	97
Pounds.....	.004	.0085	.013	.017	.026	.037	.055	.062	.080	.105	.138	.142	.181	.188





solution. The temperatures of both solutions are 70° F. There is no static head of one solution over the other. While these figures will undoubtedly vary according to the nature of the diaphragm, yet they represent well-known tendencies. These figures are also taken from asbestos such as is used in practice in making diaphragms.

It will be seen from Fig. 2 that the diffusion of caustic into the anode compartment increases very rapidly with the concentration. In order to lessen this diffusion of caustic in cells of the submerged diaphragm type it has been customary to keep the brine in the anode compartment at a higher level than in the cathode compartment, thus retarding the inward diffusion of caustic by the outflow of brine. In addition to the above it has been customary to reduce the concentration of caustic in the cathode compartment by the addition of water. This adds to the evaporating cost but more than compensates for this by increasing the efficiencies of the cells and reducing the loss of the carbons. I think we can illustrate this loss by the following equations which take place in the anode compartment.

$$2Cl + 2NaOH = NaOCl + NaCl + H_2O.$$

The sodium hypochlorate may be electrolyzed as follows:

$$H_2O + NaOCl = NaOH + H + O + Cl.$$

$$C + 2O = CO_2$$

It will be seen that this nascent oxygen attacks the carbons with the formation of carbon dioxide and heat. Thus we have a serious waste of carbons as well as a loss of power.

The diffusion of caustic also tends to increase as the temperature rises. See Table II*a* illustrated by the broken line on Fig. 2.

TABLE II*a*

Pounds NaOH Diffused per Square Foot of Diaphragm per Hour, into 26% NaCl at Varying Decomposition Efficiencies

Temperature NaOH..... 120°
Temperature NaCl..... 74°

Per Cent Decomp. Eff....	11.2	20.0	30.3	39.9	49.9	59.8	69.9	79.6	89.8
Pounds.....	.0254	.0566	.0758	.0967	.1237	.1591	.2113	.2483	.3023

The broken line shows the same factors as the solid line, with the exception that the caustic solution is at 120° F. instead of at 70° F. The brine temperature has been kept at 70° as in the first case mentioned. It will be seen from this curve that a rise in temperature in the cathode compartment increases markedly the rate of diffusion of caustic into the 26% brine solution. To illustrate this tendency still further I submit Table II*b* illustrated by the dotted line in Fig. 2.

TABLE II*b*

Pounds NaOH Diffused per Square Foot of Diaphragm per Hour, into 26% NaCl at Varying Decomposition Efficiencies

Temperature NaOH..... 120°
Temperature NaCl..... 120°

Per Cent Decomp. Eff.....	10.0	19.4	30.2	40.0	49.8	59.0	70.5	80.3	89.9
Pounds.....	.0451	.0765	.0968	.113	.147	.229	.258	.293	.346

The dotted line shows the same factors as the solid line, with the exception that both the caustic and brine solutions are kept at 120° F. It will be seen from the above that anything which tends to reduce the temperature tends to slow down the diffusion of caustic. Cells with submerged diaphragms should not be insulated against loss of heat.

I might add that the addition of water to the cathode compartment of a submerged cathode cell tends to lower the temperature of the cathode electrolyte and thus also tends to check the diffusion from this cause in addition to checking the diffusion by lowering the concentration of the electrolyte.

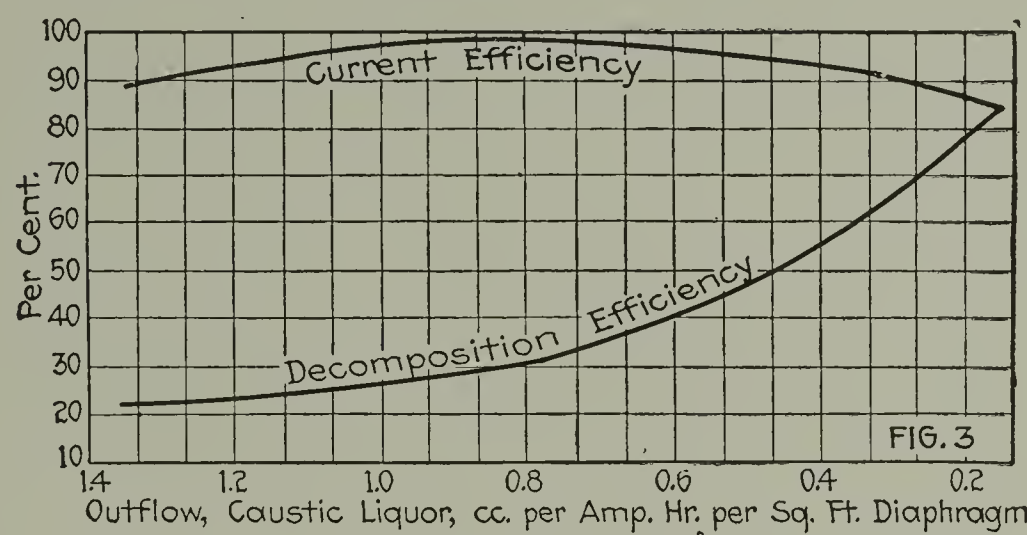
It must not be thought from what has been said above that the losses caused by diffusion of caustic into the anode compartment ended with those mentioned. In the old days gas retort carbon was the only carbon available for electrolytic purposes as Acheson's remarkable product had not then been invented. I might add that as far as I know, I was the first user of Acheson's graphite in electrolytic cells. The retort gas carbon anodes used prior to Acheson's invention were rapidly attacked by the nascent oxygen liberated on them and the mixture of carbon dioxide and chlorine went to bleach chambers where the carbon dioxide having a greater affinity

for the slaked lime than the chlorine, liberated from the bleach already formed. In order that the bleach should not test below 35% available chlorine, it was necessary to skim the carbonate of lime crust formed on the top of the bleach, from the bleaching powder underneath. Thus you see this diffusion of caustic caused not only a waste of electrolytic carbons and power but it also caused a waste of lime chlorine and labor. There were also other losses but I will not go into them here. Graphite carbons are also attacked by the nascent oxygen liberated thereon, though not to the same extent that gas carbons are attacked.

Realizing all these difficulties Moore and Allen attempted to do away with this diffusion by allowing the caustic to run away as fast as formed, either through oil or otherwise.

In experimenting with different cells it was noticed that sometimes the current efficiency of a cell starting up was usually lower than after the cell had been running a day or two. It was also noticed that as the cell got older the current efficiency generally rose for a short period, after which the current efficiency gradually declined. These results were not apparent at first because they were obscured by a varying current. In studying the reasons for this we tried to adopt a standard unit of measure by which the operation of two cells might be compared, irrespective of their ages, sizes and the current passing through them. Mr. C. B. Barton suggested the measure which we now term as the Rate of Flow and Mr. Barton and Mr. Moore, working independently, made many experiments developing this measure so that they had absolute control of the efficiency of any cell. The pounds caustic solution, per ampere hour, per square foot of diaphragm, was called the Rate of Flow. Since then this term has been broadened to include volume as well as weight. The tabulation and plotting of results showed that when the rate of flow was large the current efficiency was low because of the large amount of chlorine dissolved in the brine, which, on passing through the diaphragm with its equivalent amount of caustic and hydrogen to re-form salt and water with the liberation of heat. As the rate of flow diminished the amount of chlorine passing through the diaphragm diminished and the current efficiency rose to its maximum. As the rate of flow continued to diminish the current efficiency diminished and continued to diminish. I should like to be able to submit the original tables and charts illustrating this fact but cannot do so as they were destroyed by fire.

Table III, illustrated by Fig. 3, gives an idea of one form of rate of flow, viz., Cubic centimeter outflow caustic liquor per ampere hour per square foot of diaphragm.



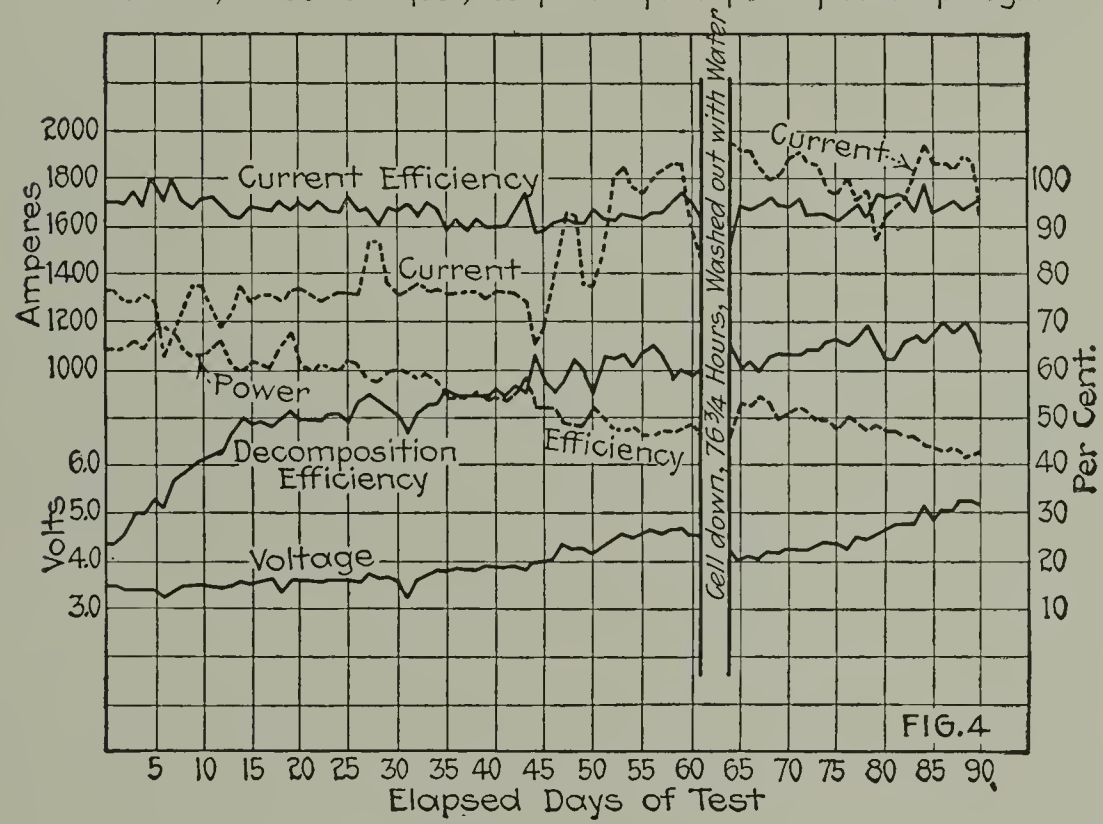


TABLE III

Shows Relation between Rate of Flow in Cubic Centimeters per Ampere Hour per Square Foot of Diaphragm and Current Efficiency and Decomposition Efficiency

Rate of flow	1.3	1.2	1.1	1.0	.9	.8	.7	.6	.5	.4	.3	.2
Current Eff.	90	93	95	97	97.5	98	97.5	96.5	94.5	92.5	90	87.5
Decomp. Eff.	22.5	23.5	25	26.5	28	32	34.5	40.0	47.0	55.5	67.5	77.5

Table IV, Fig. 4, shows a chart of a cell in which the abscissa represent consecutive days while the ordinates represent the per cent

TABLE IV

Days.	Voltage.	Current Ampere.	Current Efficiency.	Decomposition Effi.	Power Efficiency.
1	3.44	1332	95.0	23.0	63.6
2	3.39	1298	94.5	24.6	64.1
3	3.37	1282	96.5	30.5	65.8
4	3.39	1307	93.7	30.1	63.6
5	3.38	1285	100.0	32.8	68.1
6	3.24	1036	94.8	30.5	69.4
7	3.34	1128	99.3	36.9	68.4
8	3.43	1266	95.1	39.1	63.8
9	3.44	1346	93.9	40.1	62.8
10	3.47	1350	95.2	41.3	63.1
11	3.44	1233	96.3	41.8	64.4
12	3.44	1164	99.0	43.2	66.2
13	3.48	1225	92.0	46.6	60.8
14	3.55	1368	91.5	49.7	59.2
15	3.52	1282	94.4	48.5	61.8
16	3.55	1305	93.6	49.1	60.6
17	3.57	1319	93.1	48.9	59.2
18	3.32	1282	94.7	49.6	65.6
19	3.58	1326	93.3	50.8	58.3
20	3.59	1335	94.9	49.8	60.8
21	3.59	1301	92.7	49.8	59.4
22	3.55	1275	94.3	49.8	61.2
23	3.58	1300	93.1	50.6	59.8
24	3.59	1321	92.4	50.6	59.2
25	3.59	1316	96.0	49.5	61.5
26	3.56	1309	93.1	53.9	60.2
27	3.71	1531	93.5	54.8	58.0
28	3.61	1535	90.0	53.4	57.3
29	3.63	1351	94.0	51.9	59.5
30	3.59	1309	93.5	50.2	60.2
31	3.16	1328	93.6	47.0	59.5
32	3.57	1351	91.1	50.6	58.7
33	3.70	1320	94.0	52.5	59.0
34	3.76	1330	93.5	53.2	57.2
35	3.79	1309	89.4	55.2	54.3
36	3.82	1307	90.6	54.9	54.5
37	3.80	1319	89.1	54.1	54.0
38	3.81	1315	91.1	54.9	55.0
39	3.84	1296	89.1	54.5	53.4
40	3.86	1328	90.1	55.9	53.8
41	3.85	1316	90.1	54.9	53.8
42	3.89	1306	93.0	56.4	55.0
43	3.82	1152	97.3	55.2	58.6
44	3.95	1275	88.7	63.4	51.7
45	3.95	1197	88.7	58.5	51.8

TABLE IV—*Continued*

Days.	Voltage.	Current Ampere.	Current Efficiency.	Decomposition Effi.	Power Efficiency.
46	4.01	1420	90.3	54.9	51.9
47	4.31	1568	91.4	57.2	48.8
48	4.29	1634	90.4	66.6	48.5
49	4.29	1350	90.2	59.0	48.2
50	4.19	1349	93.1	60.3	51.1
51	4.27	1509	91.6	62.8	49.3
52	4.40	1812	90.8	62.5	42.5
53	4.51	1854	92.9	62.6	47.4
54	4.49	1765	91.8	61.8	47.0
55	4.53	1724	91.3	63.8	46.1
56	4.63	1791	92.1	65.4	45.7
57	4.57	1842	93.0	62.6	46.8
58	4.64	1860	95.0	58.0	47.0
59	4.68	1848	96.6	60.3	47.5
60	4.52	1598	94.8	58.9	48.2
61	4.50	1428	90.7	60.5	46.3
62	Cell down for washing diaphragm				
63					
64	4.25	1955	84.9	60.5	45.9
65	4.05	1905	93.9	60.0	53.3
66	4.10	1908	93.3	61.2	52.5
67	4.05	1831	94.8	59.9	53.8
68	4.17	1798	95.8	62.2	52.8
69	4.19	1808	94.7	63.0	49.4
70	4.25	1889	94.2	63.1	51.0
71	4.27	1918	95.9	63.3	51.7
72	4.25	1854	92.5	64.1	50.1
73	4.31	1841	92.8	64.5	49.5
74	4.35	1755	92.0	65.6	48.6
75	4.35	1721	90.7	66.0	47.9
76	4.27	1808	92.5	65.9	49.8
77	4.47	1690	94.6	66.3	48.6
78	4.46	1750	91.7	69.3	47.2
79	4.57	1524	96.4	66.4	48.6
80	4.64	1644	95.6	61.7	47.5
81	4.72	1690	96.1	62.2	46.0
82	4.79	1720	95.7	66.3	46.0
83	4.78	1841	95.5	66.7	46.0
84	5.12	1947	98.8	65.2	44.4
85	4.87	1856	92.7	67.6	43.8
86	5.06	1852	94.0	69.6	42.8
87	5.05	1821	94.8	68.4	43.2
88	5.24	1896	93.8	69.5	41.2
89	5.21	1861	94.6	67.6	41.8
90	5.15	1617	95.5	62.7	42.6

current efficiency, per cent decomposition efficiency, per cent power efficiency and the current in amperes and volts. It will be seen that a chart of this sort requires considerable study before much information is obtained.

Some of the facts shown in Table IX, illustrated by Fig. 4 are shown in Table III and Fig. 3.

It will be seen from the above that we get very regular curves from the apparently heterogeneous matter as shown on Chart IV illustrated.

Table V, Fig. 5, shows some of the lower ranges. This is only of academic interest, as cells are not supposed to run commercially in such a manner as to give such results. Of course such results as given below were obtained solely to get some idea as to what effect the continued drop in Rate of Flow would have.

TABLE V

Rate of Flow, cc.	0.8	0.7	0.6	0.5	0.4	0.3	0.2
Per cent current efficiency	95.5	94.0	91.0	86.5	81.0	75.0	67.5
Per cent decomposition efficiency	26.5	30.0	35.0	41.0	50.0	60.0	74.0

It will be noticed that Fig. 5 has different characteristics than Fig. 3. In Fig. 5 the cell was run on impure brine. It will be seen from the above that while the rate of flow chart is very valuable for comparative purposes when conditions are alike, that care must be taken not to use the rate of flow chart determined under one set of conditions to interpret results of cells run under radically different conditions.

Of course neither these results nor the above are absolute, as they may vary within certain limits as will be seen later.

In the above it will be seen that I have given number of cubic centimeters per ampere hour instead of pounds per ampere hour. This is more convenient, inasmuch as one can use a graduate instead of a set of scales.

The application of this kind of chart to the operation of a cell plant is a very simple matter. Suppose for instance you find you are going to have available in your cell plant 1000 amperes and each cell has 20 square feet of diaphragm and that you wished to run at 50% decomposition efficiency. You would look up the Rate of Flow in cubic centimeters per ampere hour per square foot of diaphragm

for 50% decomposition efficiency which according to Fig. 3 would be .46, multiply by 20 and 1000 and you have 9200 the number of cubic centimeters per hour which must run through the cell to give you your desired results. If, however, all your cells had the same number of square feet of diaphragm you could make a table like Table VI, illustrated by Fig. 6, and thus avoid the extra calculations.

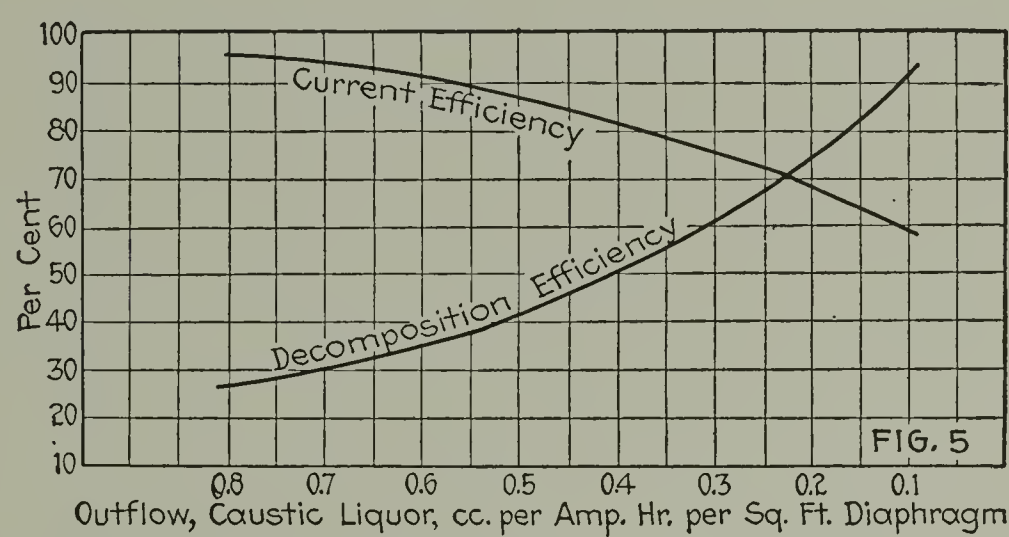


FIG. 5

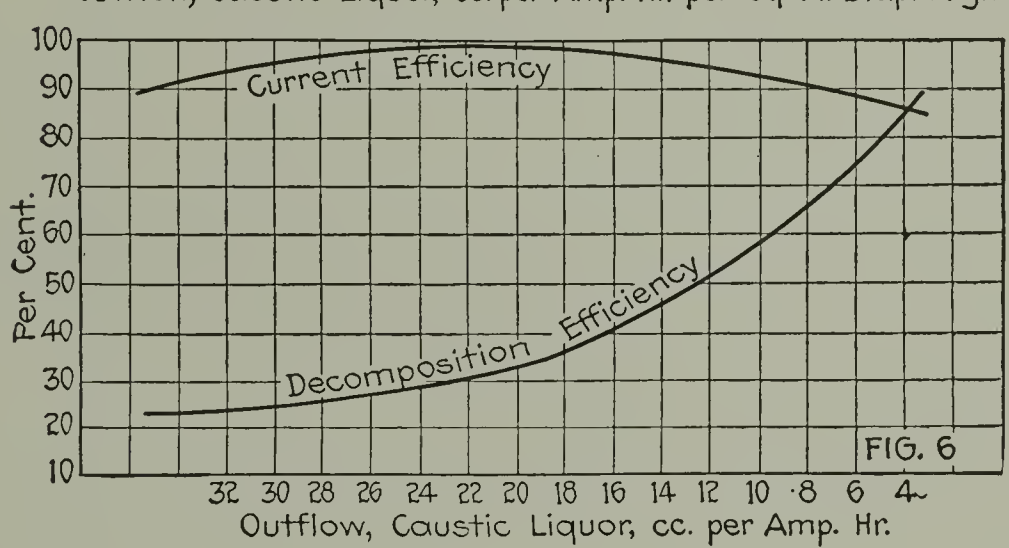


FIG. 6

TABLE VI

Rare of flow, cc. . . .	33.0	30.0	27.5	25.0	22.5	20.0	18.0	16.0	14.0
Current Eff. %. . . .	91.5	94.5	96.5	97.5	98.0	98.0	97.5	96.5	95.5
Decomp. Eff. %. . .	23.0	24.0	25.5	27.0	29.0	32.0	35.5	39.5	44.5

Rate of flow, cc.	12.0	10.0	9.0	8.0	7.0	6.0	5.0	4.0
Current Eff. %.	93.5	97.0	91.0	90.0	88.5	87.5	86.5	85.0
Decomp. Eff. %.	50.5	58.0	61.5	65.5	70.0	74.5	79.5	84.5

Fig. 6 is based on a cell having 26.5 square feet of diaphragm.

Suppose you had a cell plant each cell of which had 26.5 square feet of diaphragm and you wished to run at 55% decomposition efficiency with 1200 amperes current, you would tell the operator to so regulate the levels of the brine in the cells so that he shall obtain a flow of 216 cc. per minute, viz., rate of flow at 55% decomp. = 10.8 cc.

$$\frac{10.8 \times 1200}{60 \text{ (min. per hr.)}} = 216 \text{ cc. per min.}$$

At this decomposition efficiency the cell should have a current efficiency of 93%. It will be seen from the above curves that a cell plant cannot be regulated by the amount of brine fed to the whole plant, for the cell which has too great a flow will have a low efficiency as well as the cell which has too small a rate of flow. To run a cell plant properly each cell should be regulated as to its rate of flow individually. In a commercial plant you have a mixture of cells whose ages since renewal of diaphragms, carbons, etc., may vary all the way from one day to three hundred days. In our plant of 550 cells the ages vary from one day to one hundred and eighty days.

There has been a great deal said and written about the merits of this cell and that cell but little said about the use and abuse of cells in general or cells of the same type.

It thus happens that the exponent of one make of cell can take data from a plant using his cell running under favorable conditions and compare this with data taken from a plant using his competitor's cell running under unfavorable conditions. Neither of these statements give the buyer the exact truth, though they may help to sell the product, inasmuch as the purchaser may be fooled into accepting these statements as representative of what may be expected of different makes of cells, when in most cases differences in the results can be more than accounted for by methods of operation.

Suppose an exponent of one cell goes to a would-be purchaser of some cell and gives (*A*) the following line of talk: "Come and visit our plant at Y—— and look at our records. You will find these cells running in a voltage of 3.4 to 3.6, amperes 1220, current efficiency 95–97%, decomposition efficiency 52%, average power efficiency of 63%, age of diaphragm 280 days, life of carbons 16 to 18 months, etc., etc. If you will go to town W—— you will find an installation of our competitor's cells. You will find this plant running with cells having a voltage ranging from 3.3 to 4.7 or at an average of 4 volts. The current efficiency varies from 97% on some cells to 66% on others.

The current varies from 1200 to 1800 amperes with a power efficiency varying from 67% to 29% averaging perhaps 48%, that the age of the diaphragm in this plant is 84 days and that the life of the carbons is 4 months."

With two statements before him like this he would undoubtedly take the cell represented by Plant Y——, especially if he knew nothing about electrolytic cells and their operation. And yet, he may be very far from the truth. Do you know that the method of operation in two installations of the same cell can and does make greater differences than those stated above? One plant may be able to run their installation with a non-varying current density at the cathode

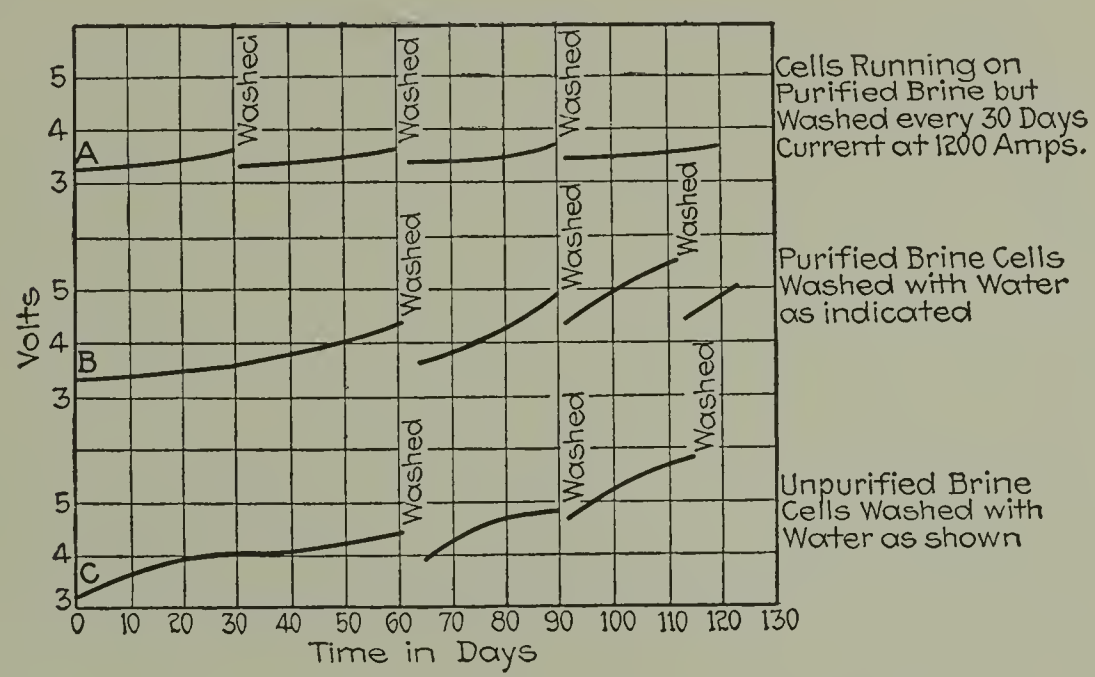


FIG. 7.—Effect of Washing on Voltage.

while another plant finds that owing to conditions of varying load on other parts of the line that it can not furnish a constant current. One operator may not see the necessity of purifying his brine while another may. These conditions alone will make startling differences in the results obtained.

To show this, I submit Fig. 7 with curves A, B, and C. (A) is a cell run constantly at 1200 amperes current, with purified brine and with the diaphragm washed with water for a period of 24 hours once every 30 days. (B) is a cell running on purified brine, with amperage varying from 1200 to 1900. The varying voltages in this and also Chart (C) have been adjusted by means of a correction chart to 1200 amperes. In this case washings were made at the end of 61 days, at the end of 90 days and at the end of 113 days. Curve (C)

is a case where a cell running on impure brine has been washed at the end of 61 days, 90 days and 115 days. Curves A and B are on cells of purified brine.

In Curve C unpurified brine was used. In order that there may be no misunderstanding in relation to the salt and brine I give the following compositions and in considering Curves A, B, and C, Fig. 7 you will consider that the brine does not vary from what is given here.

For example, let us take a salt which analyzes as follows:

Insoluble matter	.40
$CaCl_2$	.36
$MgCl_2$	trace
$CaSO_4$	.70
NaCl	98.54
	100.00%

With brine made up $2\frac{1}{2}$ pounds to the gallon we get from the above:

	Grams per Liter.
Insoluble matter	1.20
$CaCl_2$	1.08
$MgCl_2$	trace
$CaSO_4$	2.10
NaCl	285.62
Total grams other than water per liter	290.00

After adding soda ash to about 1% excess of the requirements filtering and neutralizing with HCl we get a solution of the following composition:

	Grams per Liter.
Insoluble matter	none
$CaCl_2$	none
$MgCl_2$	trace
$CaSO_4$	heavy trace
Na_2SO_4	2.20
NaCl	286.76

Now let us see the results of feeding the above-mentioned impure brine to a cell and compare these with the results obtained from the purified brine.

It will be observed that in (C) the voltage rises to 3.6 at the end of 10 days while in Charts A and B the voltage does not rise to 3.6 until 30 days. If now the cells running on purified brine are washed at the end of 30 days for 24 hours, with water, it will be found upon starting up the voltage will have dropped to somewhere between 3.3. and 3.4. In the case before you the voltage upon starting up was 3.3. If the cell is again washed at the end of another 30 days or less we will have a similar drop though slightly less.

Curves B and C may be misleading unless certain explanations are made. It will be noticed that after 30 days the voltage goes up at a faster rate than at the beginning of this period. This is due to some extent to the accumulation of impurities during the 30-day period but in the main this is due to the great increase in impurities in the diaphragm due to excessive amperage. During this time the amperage was uniformly higher than 1200 amperes going at times to nearly 2000 amperes. Consequently more brine had to be fed to the cells in a given time with the consequent increase of impurities in the diaphragm. While the voltage has been corrected for excessive amperage it has not been corrected for these accumulated impurities. Compare Curve C which represents a cell running under the same conditions as that in Curve B with the exception that the brine is not purified. It will be noticed that the curve rises very rapidly at the start but flattens out as the age increases. This is due to the fact that with more impurities in the brine the plugging of the diaphragm was greater and the liquor in the cell rising to its limit automatically checked the inflow of liquor coming in through the float valve. Now cells represented by Curve C started in at an initial flow of 21.00 cc. per ampere hour (1200 amperes 26.5 sq. ft. of diameter) and at the end of 10 days the flow in spite of the increasing static head had been reduced to 7 cc. per ampere hour, or only one-third as much as at first. A flow of about 9 cc. per ampere hour is good practice. Cell represented by C has had its diaphragm plugged so rapidly that the diaphragm should have been washed at the end of ten days and this washing would not have been entirely satisfactory.

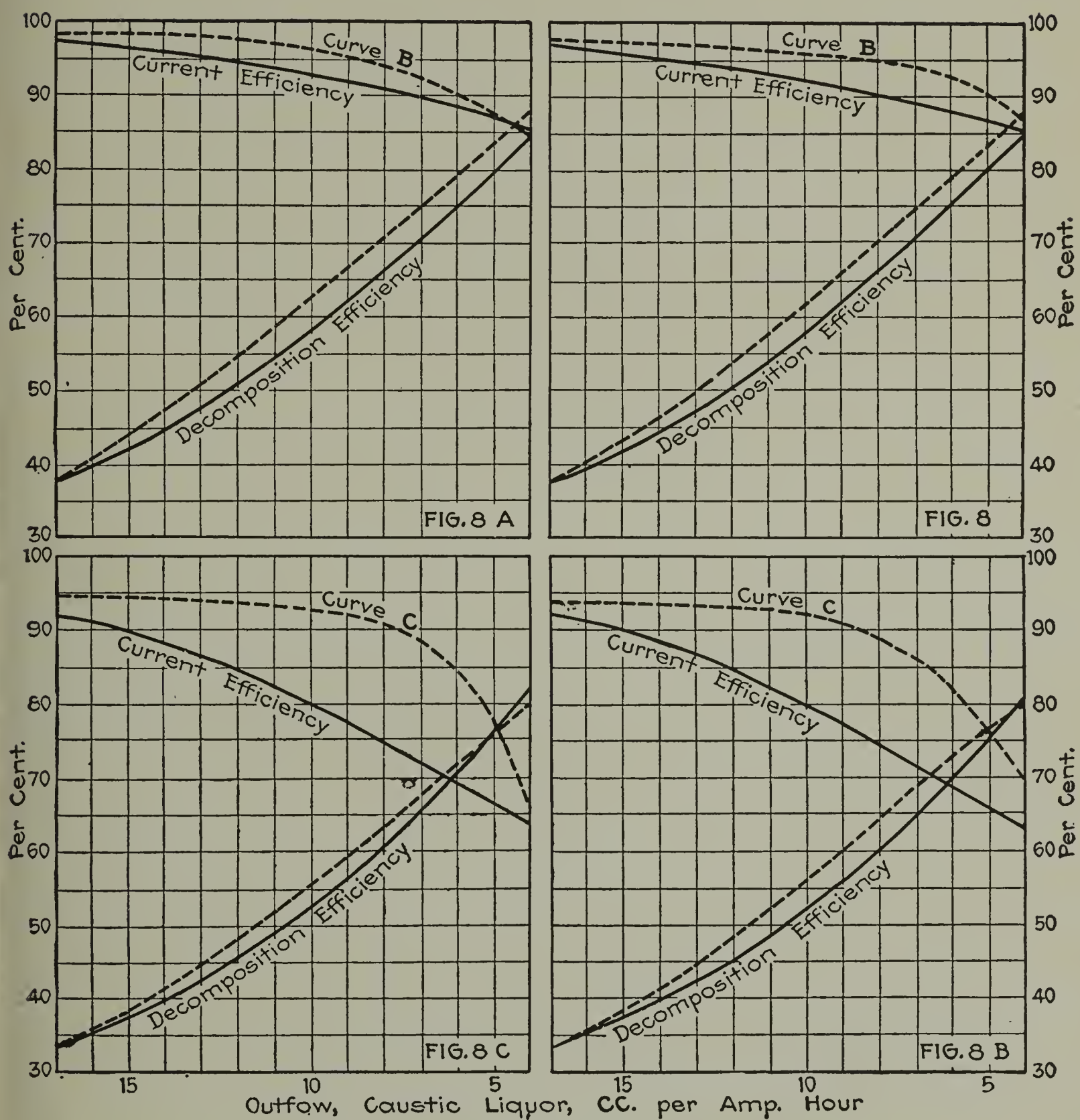
Now cells represented by Curves A and B start in with an initial rate of flow of 30 cc. per ampere hour and at the end of ten days without any raise of static head, drop to a rate of 15 cc. per ampere hour. From the above you would naturally expect a flat voltage curve on curve B as there are few impurities and the flow is so rapid

that one would expect that they would lodge only to a small extent in the diaphragm. You would also expect a rapidly rising voltage curve on Curve C as we have here all the impurities and the flow is so reduced that they must lodge in the diaphragm.

I wish to bring out another fact oftentimes not appreciated and that is that washing the diaphragm not only saves the cost of a new diaphragm together with the labor needed to change the same but that the washed diaphragm is actually a better diaphragm than a new diaphragm. In order to show this I submit Fig. 8 corresponding with Curve B on Fig. 7 showing the effect the washing has on the current efficiency. The ordinates are current efficiencies and decomposition efficiencies and the abscissæ are cubic centimeters of flow per ampere hour. The heavy black line shows efficiencies in terms of the rate of flow in cubic centimeters per ampere hour on a diaphragm which has not been washed out. The dotted line shows the change in current efficiency on same diaphragm after washing with water. It will be noticed that the current efficiency and decomposition efficiency is raised for the same rate of flow in both cases.

If you refer to Fig. 8*a* representing Curve B, Fig. 7 you will see the effect of the second washing. The heavy black line representing the same facts as in Fig. 8. Similarly Fig. 8*b* and Fig. 8*c* corresponding to Curve C shows that both the current efficiency and decomposition efficiency are raised for the same rate of flow for both efficiencies by washing with water. I have many such charts of cells run under many different conditions and find that practically all show this characteristic. In order that the information contained in the above may be available to users of cells having varying diaphragm area I will state that these areas of diaphragm in the above cases were 26.5 square feet each. I should like to give more time to this subject but must drop it at this point in order to take up other subjects. I cannot, however, let the matter drop without giving at least one illustration as to how Curve A may be carried out in practice. I submit Table VII taken from Dill & Collins Plant, July 19, 1919.

It will be noticed that no cell had been changed for 49 days, while the oldest cell was 248 days. It will be noticed that certain cells show an efficiency of over 100%. These are errors which may occur in various ways. The low efficiencies may also be errors. The average efficiency is undoubtedly correct. I shall discuss later some of the factors contributing to calculations of current efficiency in an



FIGS. 8, 8A, 8B, and 8C.—Current and Decomposition Efficiencies, Dashed Lines after First Water Work and Solid Line Before Water Work.

TABLE VII

ELECTROLYTIC PLANT OF DILL AND COLLINS

July 19, 1919

Current Amperes 1200

Cell No.	Days Run.	Voltage.	Per Cent current Eff.	Liters per hour	Cell No.	Days Run.	Voltage.	Per Cent current Eff.	Liters per hour
1	151	3.50	102.2	17.6	32	169	3.70		
2	195	3.50	96.3	15.4	33	157	3.60		
3	125	3.50	95.5	15.6	34	172	3.65		
4	201	3.50	91.2	13.0	35	170	3.55		
5	171	3.55	100.6	18.6	36	199	3.50	91.4	18.6
6	168	3.50	102.6	17.0	37	163	3.50	91.4	18.6
7	145	3.60	93.0	14.4	38	120	3.50		
8	201	3.50	94.8	13.6	39	174	3.50	89.4	18.6
9	146	3.50	101.3	18.0	40	146	3.60	90.0	16.4
10	104	3.66	104.6	15.0	41	184	3.60	94.1	14.8
11	201	3.60	94.4	17.6	42	168	3.55	95.5	17.8
12	168	3.50	96.2	17.8	43	168	3.60	99.0	16.1
13	49	3.50	95.2	14.6	44	168	3.50	94.2	17.0
14	117	3.60	98.8	17.0	45	140	3.50	92.3	17.2
15	191	3.55	96.8	17.2	46	196	3.60	86.7	15.0
16	192	3.65	91.5	16.0	47	143	3.60	93.6	17.0
17	156	3.50	106.6	15.6	48	219	3.55	100.4	18.8
18	146	3.60	94.1	17.4	49	196	3.60	116.8	19.8
19	168	3.50	98.3	16.0	50	191	3.50	95.2	17.6
20	109	3.55	97.6	14.8	51	177	3.55	94.8	14.6
21	141	3.50	91.5	15.4	52	173	3.65	96.7	15.4
22	192	3.50	96.4	17.4	53	191	3.65	90.5	16.2
23	119	3.60	95.9	15.6	54	174	3.55	93.8	17.8
24	154	3.60	95.2	14.8	55	227	3.50	94.8	15.6
25	196	3.60	92.0	16.6	56	248	3.55	92.0	12.4
26	199	3.60	95.2	15.2	57	97	3.55	90.7	17.0
27	173	3.60	97.8	19.2	58	186			
28	166	3.55	.....	.....	59	94	3.60	93.4	16.2
29	170	3.45	.....	.....	60	191	3.50	96.1	12.8
30	173	3.55	.....	.....	61	177	3.55	87.8	14.4
31	171	3.65	.....	.....	62	120	3.60	93.4	16.2

Average run in days = 165
Average voltage = 3.55
Average current eff. = 95.6
Average liters per hour = 16.3
Current held at 1212 amperes.
Decomposition efficiency held as close to 50% as possible.

(.....) Cells had been shut down to wash and had just started up so efficiencies had not been taken.

electrolytic cell. But right here I wish to mention a factor which will show why even though the high and low figures may be wrong the average of the total may be correct. In testing for the current efficiency of a cell the amount of caustic liquor which runs off in a given period of time is tested for caustic soda and the current efficiency calculated from the above and the number of amperes passing through at the time. Now if due to evaporation there is an accumulation of salt in the outlet pipe, we would have a slight damming up of caustic in the cathode chamber and we would be getting a less amount of caustic liquor than actually flowed through the diaphragm and consequently the current efficiency for such cells would show lower than the actual. If on the other hand the salt which had partially obstructed the flow of caustic liquor should dissolve out while the test is being taken, the flow from the cell would be greater than the flow through the diaphragm and consequently the current efficiencies for such cells would show higher than they actually are. The caustic solution is always unsaturated as regards both caustic and salt so that the obstructions are bound to dissolve out. Of course the longer the test, the less will be the effect of such disturbances. Of course if long tests are taken the efficiencies of all the cells can not be taken at one time. So the short cell test has a certain advantage even though there may, in a few cases, be a small inaccuracy. On a large number of cells it has been found that the increasing flow in some cells compensates for the decreasing flow in other cells, so that the average efficiency for all the cells checks with the efficiency of the plant. Consequently, with this explanation it is better to submit all the figures as taken than to take the risk of rejecting the high and low figures.

The decomposition efficiencies are not tabulated, but each cell is run as close to 50% decomposition efficiency as factory operation will allow. This table is not a selected table but one which was taken on the date when two of my representatives happened to visit the plant. This is especially instructive in showing how systematic washing of cells combined with efficient management can keep cells from deteriorating. Dill and Collins' plant will show results comparable to the above any day in the year. I have been informed that the carbons in this plant last from 16 to 18 months.

Compare the life of the carbons in a plant run as above with the life of carbons in a cell using impure brine as in Curve C, Chart VII. In this case the carbons other than the spacing blocks were used up

in less than 120 days. In cells represented by Curve B the carbons were whole and good for a considerable extension of time.

From the above it will be seen that proper care of an electrolytic cell is as important a factor as the proper care of an engine. Perhaps I can bring this more forcibly to your attention if I give some comparative figures of costs.

Assuming carbons at 22c. per pound.
Asbestos paper at $1 per pound.
1 horse-power year (24 hours a day), $40.

We find that the costs for these three items alone come to the following figures, as shown on Table VIII:

TABLE VIII

Cost per Ton Salt Decomposed.	Curve A.	Curve B.	Curve C.
Carbons	1.03	2.11	4.34
Asbestos	.38	.58	.72
Power	9.46	11.85	15.61
Total	10.87	14.54	20.67

As has been previously stated, it is possible to feed to the cells a salt solution of 99% saturation. This does not mean, however,

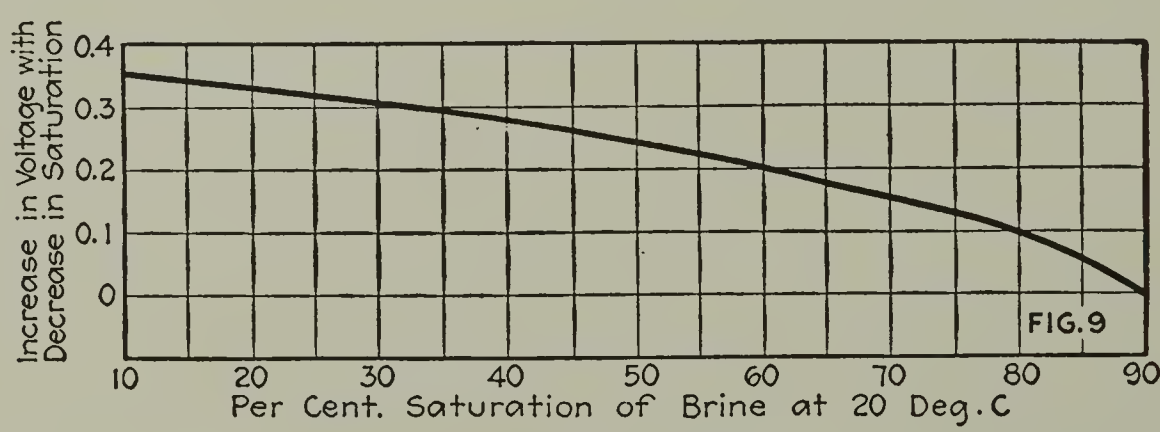


FIG. 9.—Relation of Anode Brine Saturation to Cell Voltage. Constant Temperature.

that the saturation in the inside of the cell will be 99% saturation for this is rarely the case. Most cells running at average decomposition efficiencies decompose the brine faster than it comes in. The average brine saturation in a cell running 93 to 95% current efficiency

varies from 80 to 82%. It might be interesting to see what effect the brine saturation has on the voltage of a cell. To show this I submit Table IX, illustrated by Fig. 9.

CHART IX

Showing Drop in Voltage with Increasing Saturation

Brine Saturation at 20° C.	Cell Temp. ° C.	Drop in Voltage.	Amperes.
15	28.0	.00	1200
35	27.5	.06	1200
50	27.8	.18	1200
65	28.0	.24	1200
85	27.8	.28	1200
90	28.0	.33	1200

Lowering the brine concentration in the cell not only uses up power but it tends to make the current electrolyze water with the resulting

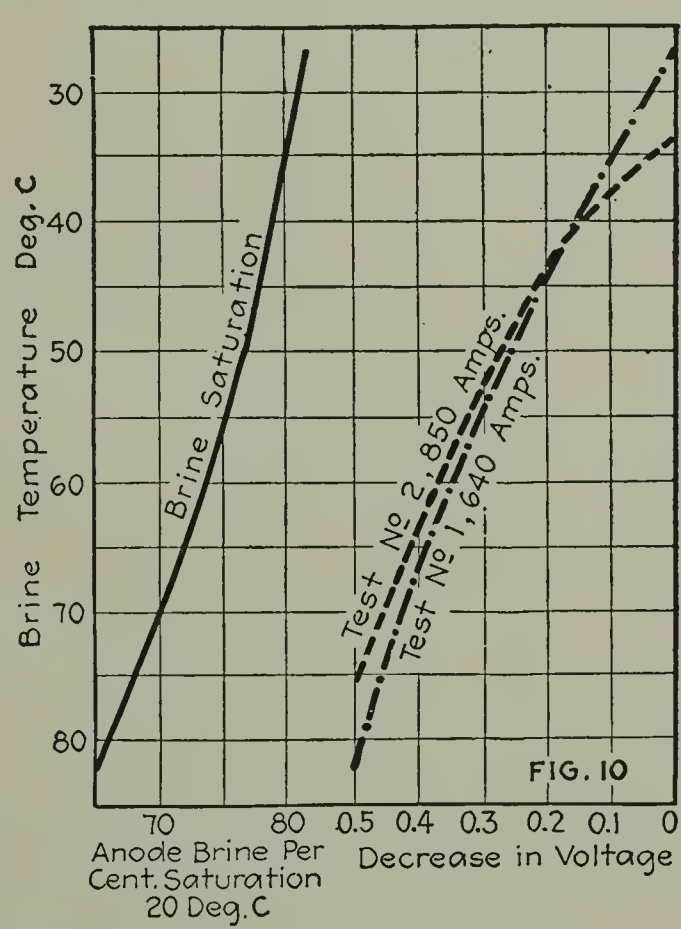


FIG. 10.—Anode Brine Temperature vs. Cell Voltage with Constant Saturation.

liberation of nascent oxygen at the anode with the consequent more rapid destruction of the carbons. I cannot take the time to go into

this now but will be content with remarking that the rapid destruction of the carbons, see Table VIII, Curve C.

It is often difficult to evaluate the effects of brine concentration because of the disturbing effect of another variable, viz.: temperature. To illustrate this I submit Table X illustrated by Fig. 10.

Table X shows brine temperature and decrease in cell voltage, decreasing brine saturation and increasing temperature.

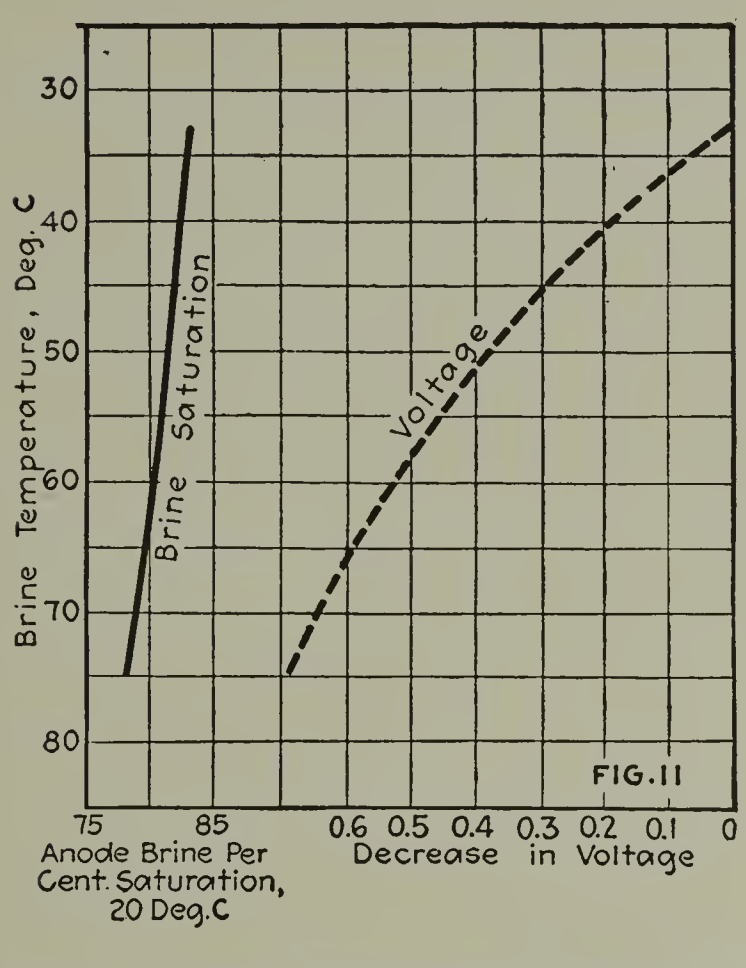
TABLE X

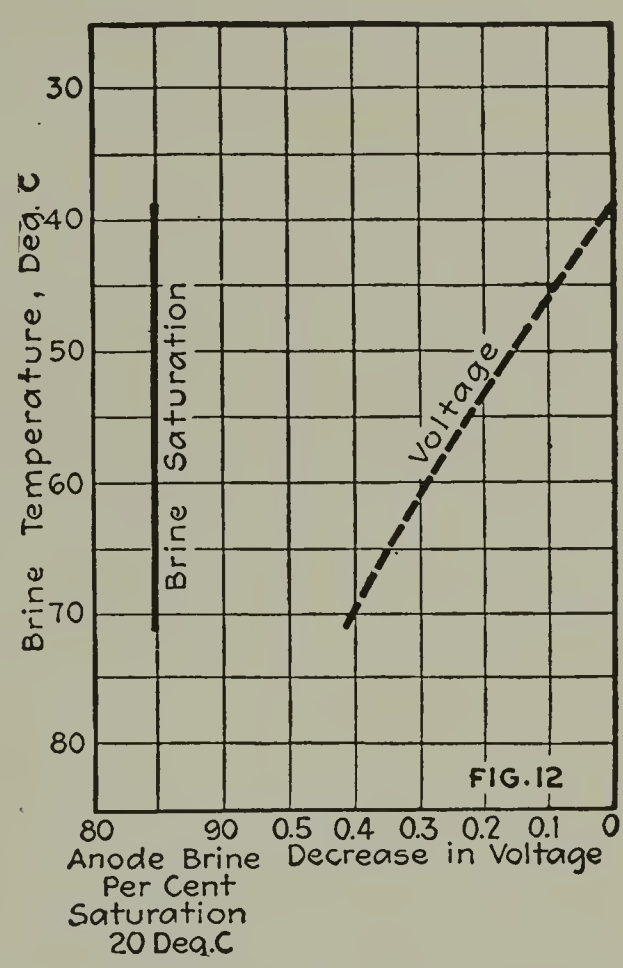
	Brine Temp.	Saturation at 20° C.	Cell Volts.	Decrease in Voltages.	Amperes.
	26.8° C.	81.5	3.40	0.50	640
	30.0	81.0	3.36	0.46	640
	36.8	80.5	3.28	0.38	640
1.	44.0	.....	3.20	0.30	640
	50.0	.....	3.14	0.24	640
	57.5	75.0	3.06	0.16	640
	68.0	70.0	3.00	0.10	640
	82.0	65.0	2.90	0.00	640
	33.5	81.0	3.70	0.80	850
	41.5	.....	3.52	0.62	850
	52.8	77.0	3.40	0.50	850
2.	48.0	.....	3.46	0.56	850
	57.5	75.0	3.34	0.44	850
	61.0	.....	3.30	0.40	850
	76.0	68.0	3.20	0.00	850

The abscissæ are temperatures in degrees C. while the ordinates show the decrease in voltage. Another set of ordinates show the per cent saturation of the brine at the varying temperature. The solid line shows the per cent saturation at 20° C. The dash line corresponds to 640 amperes while the dot and dash line corresponds to 850 amperes. It will be noted that these lines are nearly parallel showing in each case approximately the same degree of drop. The solid line is inserted into this chart to show the concentrations in this particular experiment but as the concentration and temperatures may vary independently of each other, this curve must not be used to predict a concentration at a given temperature.

In order to get the effects of temperature on voltage two experiments were conducted with the object of keeping the concentration

constant. Table XI illustrated by Fig. 11 and Table XII illustrated by Fig. 12, show the results obtained.





FIGS. 11. and 12.—Anode Brine Temperature vs. Cell Voltage with Decreasing Saturation.

TABLE XI

Brine Temperature.	Saturation at 20° C.	Cell Volts.	Decrease in Voltage.	Amperes.
33.0° C.	88.0	4.24	.69	1200
39.0	87.5	4.05	.50	1200
47.0	86.5	3.95	.40	1200
54.5	85.5	3.80	.25	1200
57.5	85.0	3.75	.20	1200
61.0	85.0	3.72	.17	1200
70.0	84.0	3.60	.05	1200
75.0	83.0	3.55	.00	1200

In each case the abscissa is the brine temperature in the anode compartment while the ordinates represent the decrease in voltage. As before, the solid line represents the concentration of the brine

TABLE XII

Brine Temperature.	Saturation at 20° C.	Cell Volts.	Decrease in Voltage.	Amperes.
39.0° C.	85.0	3.86	.41	1000
47.5	86.0	3.75	.30	1000
51.0	85.0	3.70	.25	1000
55.5	85.0	3.66	.21	1000
59.5	85.0	3.58	.13	1000
65.5	84.0	3.50	.05	1000
71.0	84.0	3.45	.00	1000

while the dash line shows the drop in voltage. The saturation in Figs. 11 and 12 has been maintained by adding solid salt. The temperatures were obtained by blowing steam into the cell.

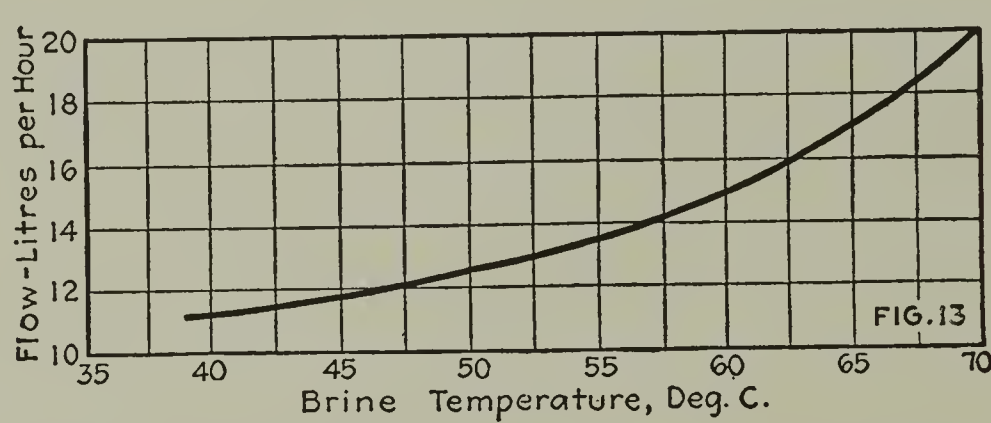


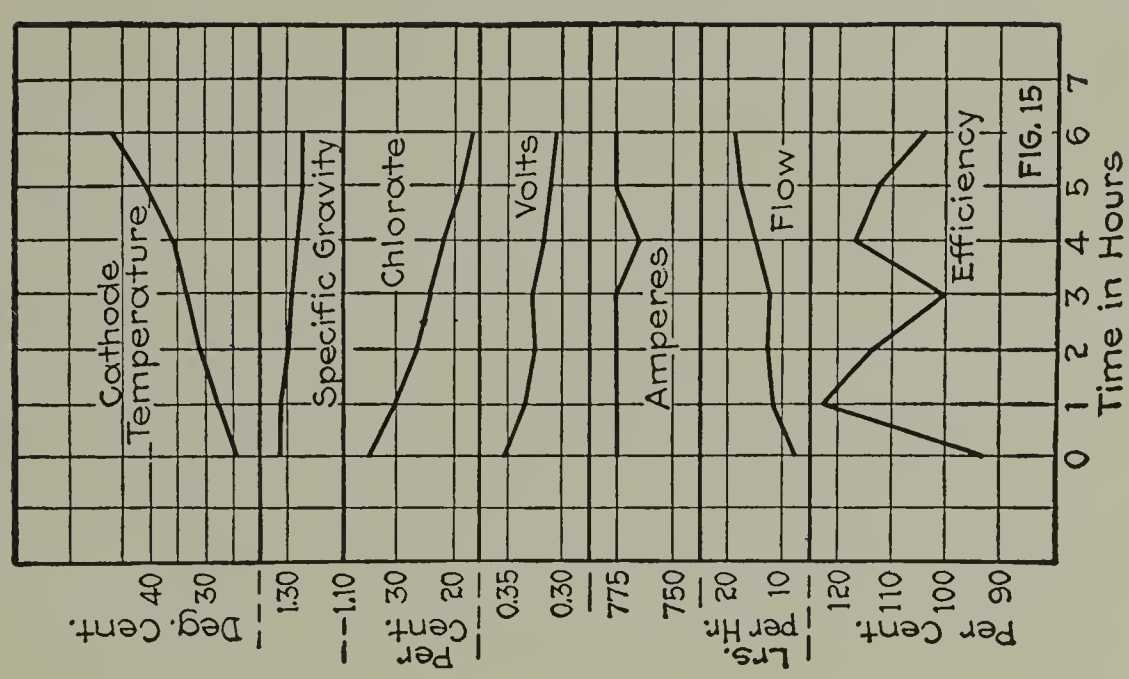
FIG. 13.—Relation of Flow from Cell to Brine Temperature.

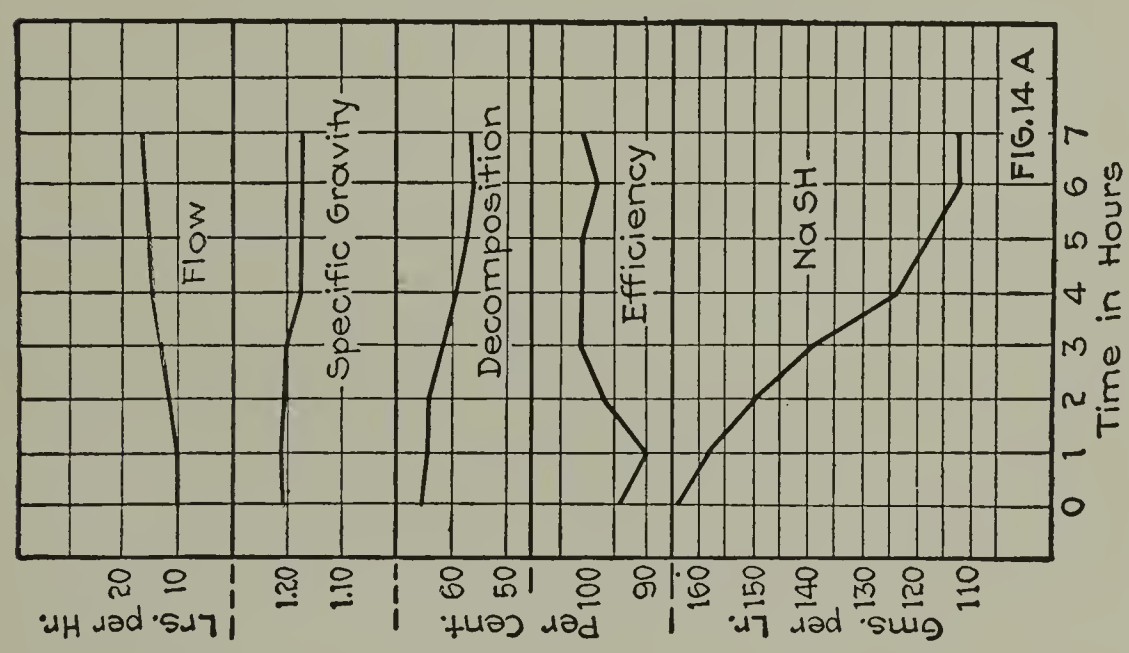
Raising the temperature in a cell also increases the fluidity of the brine and consequently it is well that we should know the effect.

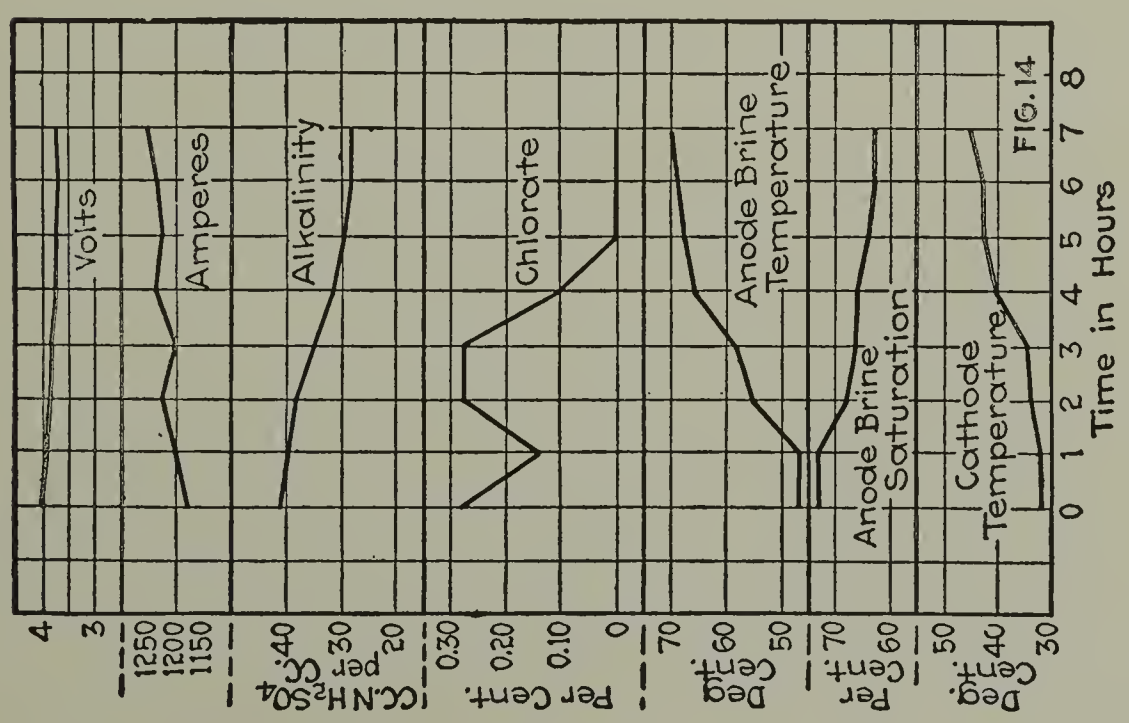
The experiments illustrated by Tables X, XI and XII were conducted on especially high voltage cells in order that the increased flow due to rise in temperature should not be so great as to modify the other characteristics too markedly.

This brings up another matter and that is the increased flow due to temperature. Table XIII and Fig. 13 show this effect in a striking manner.

In order to illustrate still further the effect of temperature on a diaphragm cell I submit Tables XIV, XV, and XVI, illustrated by Figs. 14, 15, and 16, showing the effects of blowing steam into the cell on the different factors noted.







FIGS. 14 to 15.—Effect of Steam on Allen-Moore Cell.

TABLE XIII

Brine Temperature.	Flow in Liters.	Amperes.
39.0° C.	11.7	1000
47.5	12.2	1000
59.5	14.8	1000
71.0	20.2	1000

TABLE XIV

EFFECT OF STEAM ON ALLEN-MOORE CELL NO. 43

Volts.	Amperes.	Causticity.	Gram per Liter.	Chlorate.	Anode Temp.	Anode Sat.	Cath. Temp.	Flow Liters per Hour.	Specific Gravity	Decomposition.	Efficiency.	Time.
4.0	1180	41.0	164	.28	46.5	73	32.0	10.2	1.2083	65.4	94.8	9 a.m.
3.92	1200	39.5	158	.14	46.5	73	31.5	10.2	1.2104	64.6	89.8	10 a.m.
3.8	1225	37.5	150	.28	55.5	68	34.0	11.8	1.2073	64.2	96.7	11 a.m.
3.8	1200	35.0	140	.28	58.5	66	35.0	13.0	1.2023	61.5	101.0	12 m.
3.7	1235	31.0	124	.10	66.0	66	40.5	15.0	1.1769	59.0	101.0	1 p.m.
3.7	1225	29.5	118	.00	67.5	64	43.0	15.6	1.1750	57.2	101.0	2 p.m.
3.65	1235	28.0	112	.00	68.5	63	43.0	16.3	1.1749	56.0	98.3	3 p.m.
3.7	1250	28.0	112	.00	70.0	63	45.5	16.8	1.1741	56.5	101.0	4 p.m.

TABLE XV

EFFECT OF STEAM ON ALLEN-MOORE CELL NO. 43.

Temperature.		Sp. Gr.	Chlorate.	Causticity.	Volts.	Amp.	Flow, Liters per Hr.	Eff.	Time.
(without)	24.0	1.2104	.45	35.0	3.52	775	7.5	91.9	10 a.m.
(with)	27.0	1.2063	.26	30.0	3.32	775	11.4	122.5	11 a.m.
	30.5	1.1954	.26	26.0	3.22	775	12.6	113.7	12 a.m.
	33.0	1.1866	.12	24.0	3.25	775	12.1	100.3	1 p.m.
	35.5	1.1798	0.0	20.0	3.15	775	14.90	117.0	2 p.m.
	40.5	1.1703	0.0	18.5	3.08	775	17.8	113.0	3 p.m.
	46.5	1.1675	0.0	16.0	3.02	775	18.6	104.0	4 p.m.

TABLE XVI.

EFFECT OF STEAM ON ALLEN-MOORE CELL NO. 43.

Volts.	Amperes.	Causticity.	Gram per Liter.	Flow Liter per Hr.	Decomposition.	Sp. Gr.	Anode Sat.	Efficiency.	Cath. Temp.	Time.
3.3	795	22	88	14.0	46.3	1.1820	65	102	32.5	9 a.m.
3.2	795	20	80	17.0	42.3	1.1720	65	114	36.0	10 a.m.
3.4	900	19.5	78	16.3	42.5	1.1760	65	95.2	38.0	11 a.m.
3.4	900	22	88	16.8	46.5	1.175	65	109	38.0	12 a.m.
3.5	900	24	96	13.8	50.4	1.180	65	98	35.0	1 p.m.
3.58	900	26	104	13.6	52.2	1.182	65	105	34.5	2 p.m.
3.6	900	26	104	13.2	52.3	1.184	65	100	33.5	3 p.m.

I wish to particularly call your attention to the decrease of chlorate in caustic liquor with the increase in temperature. In all probability this may be accounted for by the increased activity of the nascent hydrogen at the cathode on the decreased stability of sodium chlorate.

I have previously spoken of the possibility of getting more than theoretical efficiencies on tests of short intervals of time. I mentioned at this time one cause which would make it possible to obtain such results.

In Fig. 14 you will see another illustration of this fact but for another cause, i.e., the lag in the cell. In the case before you we have a beautiful illustration of this fact. It will be noticed that during the experiment the causticity dropped from 35 to 16 while the flow increased from 7.6 to 18.6. The above conditions always give an apparent efficiency higher than the actual and as the actual is near 100% the apparent efficiency will be over 100%. There is in every cell a certain volume of caustic held by capillary attraction in various parts of the cathode compartment. Now, if one volume of the strong caustic so held is replaced by a like volume of a weaker caustic the caustic effluent will contain more NaOH than was actually produced during the time in question.

While I am speaking of the high efficiencies of cells I might mention that the same effect will be produced if the cells run at an abnor-

mally high amperage just before a test and then drop to normal as the test commences. I have known some crooks to do the above purposely for a joint test. This causes a high efficiency due to the lag in the strong caustic getting away. Of course if these conditions are reversed you get efficiencies correspondingly low. Of course if the meters do not read correctly you get abnormal results in the same way that you do if your testing solutions are not of the strength used in your calculations.

Of course the above considerations are based on cells in which the amperage is accurately determined.

In studying Fig. 16 it will be seen that there is a rise in voltage on the second hour even though there is a rise in temperature. This is due to a rise in amperage at the same time. The volts continue to rise but it will be noticed that the temperature drops while the

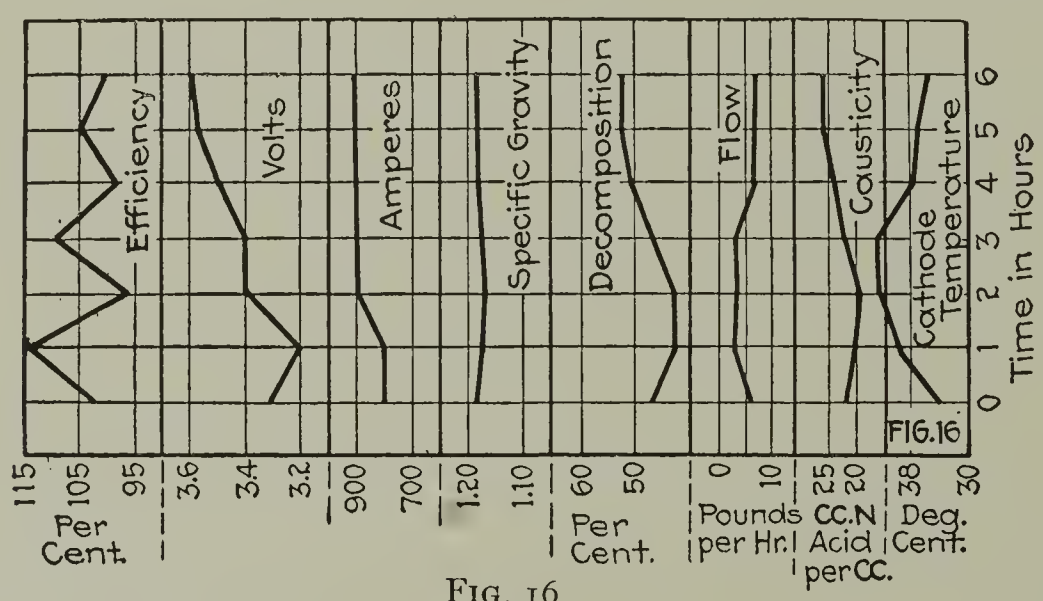


FIG. 16.

amperage remains stationary. It will be noted also that the brine in the anode compartment is only 65% saturation.

Many do not realize that small quantities of sodium sulphate in the salt fed to the cell can have a deteriorating effect on the cell itself. Experiments have shown that the absolute removal of sodium sulphate from the brine, actually decreases the amount of carbon dioxide in the chlorine gas. The presence of this carbon dioxide in the gas not only causes a loss of brine in making bleach but it indicates a deterioration of the carbons in a cell. The loss from the carbons is however much greater than one would suppose from the amount of carbon dioxide in the gas. The explanation is simple. As that carbon going into carbon dioxide is removed from the structure of

the carbon the cohesive force of other particles is lessened and they sluff off by the friction of the circulating electrolyte.

From the above one would expect that the absolute removal of sodium sulfate from the brine would increase the life of the carbons. Actual experiment has proved such to be the case. I am not, however, going to give these figures inasmuch as I have not tried enough experiments to get an average figure which I can term reasonably correct.

It might be interesting to note the increasing amount of chlorate formed in a cell of the submerged diaphragm type by the addition of a brine containing 1% and 2% sodium sulphate. Fig. 7 shows this. Inasmuch as the lag in the cell is very large and the cell had not

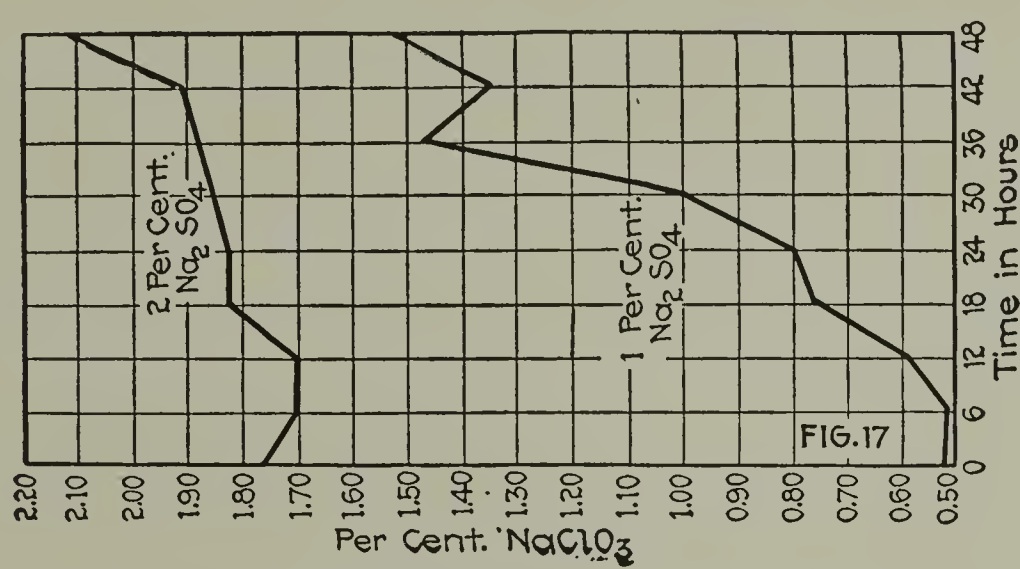


FIG. 17.—Effect of Na_2SO_4 Solution on Le Sueur Cell

reached equilibrium owing to the short time of run, I cannot give you a chart showing the per cent of chlorate which would uniformly be present for different percentages of sodium sulphate. The matter, however, is very important inasmuch as herein lies a great source of danger to say nothing of expense.

In evaporating a caustic solution it is possible, to crystallize out most of the salt but impossible to crystallize out the sodium chlorate. When the kettles containing such chlorate become heated to a sufficient temperature, the sodium chlorate is liable to explode throwing tons of molten caustic on the floor. Even if the kettles are so run that the sodium chlorate decomposes gradually and smoothly, we may have a low test caustic from the presence of sodium chloride formed by the dissociation of the sodium chlorate.

I had intended to say something in relation to wear and tear on

preservation of carbons but as this is already a long paper and inasmuch as I have not sufficient first-hand knowledge, I shall omit in this paper but give it in another paper at another time, if the members so desire.

BROWN COMPANY,
Berlin, N. H.

APPENDIX

CALCULATION OF DECOMPOSITION VOLTAGE

It was stated by Helmholtz in 1847, and W. Thompson in 1851, that in a galvanic element, chemical energy is completely transformed to electrical energy. Then if the heat of reaction in calories per gram-equivalent is called U, the electromotive force in volts which could be produced by it, E,

$$E=\frac{U}{23046}* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This is often approximately true, its error depending on the temperature coefficient of the electromotive force, and this in turn on the difference of the molecular heats of the reacting substances and the resultant substances. The theoretical basis of the correct method was established by Gibbs and Helmholtz somewhat later, but the new equations were of little use until Nernst's heat theorem was applied to the problem. The result may be written in the form:

$$E=\frac{U-2BT^2}{23046} \text{ (approx.)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Where T is the absolute temperature, in Centigrade degrees, and $B=\frac{1}{2T}$[(Specific heat of all the reactants, per gram equivalent)—

* Nernst, "Theoretical Chemistry," 6th ed., p. 733.

(specific heat of all of the resultants, per gram equivalent)]. But to apply even this expression, calculations must be made on a basis, first, of each phase being a pure solid or liquid substance; not, for instance, a solution. In the case of the ordinary electrolytic chlorine cell, for instance, the required specific heats must be known at a temperature at which the hydrogen and chlorine are liquid, and the salt and caustic are solid NaCl, $2H_2O$ and NaOH, $7H_2O$, respectively. The requisite correction to bring up the results to room temperature can then be made on the basis of the solubility-temperature curves. Such data, however, and especially the specific heats of low temperatures, are known for only a few substances. It is evident, then, that with the physical data now available, the accurate calculation of decomposition potentials is impossible.

The approximate voltage obtained by equation 1 is, in fact, commonly used in practice. The unknown correction factor may be either positive or negative, and may range from zero to three or four-tenths of a volt, or even more. In the case of the chlorine cell it is supposed to be about +0.1 volt.

The heat effects and approximate decomposition voltages of sodium and potassium chlorides in aqueous solution are given below, indicating the degree of uncertainty in each case due to conflicting determinations of heat of formation.

Substance.	Heat of Formation, M Cl=M+Cl.	Heat of Formation, $M+H_2O+Aq=MOH+H+Aq$.	Net Heat Effect. Cal. per Gram Equiv.	Decomp. Voltage.
NaCl.....	97,900 to 97,690	42,400 to 45,000	55,500 to 52,690	2.41 Av. 2.35 2.28
KCl.....	105,700 to 105,610	45,200 to 48,100	60,500 to 57,510	2.62 Av. 2.56 2.50

Theoretical Yields per Ampere Hour.

Elements

	Pounds	Grams		Pounds	Grams
Sodium	0.00189	0.858	Hydrogen	0.0000823	0.0373
Potassium	0.00322	1.459	Oxygen	0.000644	0.292
Calcium	0.00165	0.747	Chlorine	0.00292	1.322
Magnesium	0.00100	0.453	Bromine	0.00644	2.92
Iron (from Fe″)	0.00230	1.041	Antimony	0.00330	1.497
Nickel	0.00242	1.092	Tin	0.00487	2.21
Cobalt	0.00243	1.101	Bismuth	0.00572	2.59
Zinc	0.00269	1.218	Cadmium	0.00461	2.09
Lead	0.00852	3.86	Copper (from Cu″)	0.00260	1.18
Silver	0.00888	4.02	Platinum	0.00400	1.81
Gold (from Au″)	0.00540	2.45	Aluminum	0.00075	0.34

Inorganic Compounds.

NaOH	0.00329	1.492	$NaClO_3$ (from NaCl)	0.00146	0.660
KOH	0.00462	2.095	$KClO_3$ (from KCl)	0.00168	0.761
$Ca(OH)_2$	0.00305	1.382	Na_2CrO_4 (from $CrCl_3$)	0.00445	2.015
$Mg(OH)_2$	0.00240	1.087	K_2CrO_4 (from $CrCl_3$)	0.00532	2.41
ZNO	0.00335	1.518	$PbCrO_4$ from H_2CrO_4)	0.01330	6.02
Cu_2O	0.00589	2.67	$NaMnO_4$ (from Na_2MnO_4)	0.01168	5.29
PbO_2	0.00492	2.23	$KMnO_4$ (from K_2MnO_4)	0.01301	5.90
White lead (approx.)	0.00631	2.86	$Na_2C_2O_6$ (from Na_2CO_3)	0.00684	3.10
$Na_2S_2O_4$ (from $NaHSO_3$)	0.00717	3.25	$K_2C_2O_6$ (from (K_2CO_3)	0.00816	0.70
$Na_2S_2O_8$ (from $NaHSO_4$)	0.00957	4.34	NH_2OH (from HNO_3)	0.00045	0.205
$NaBO_3$ (from borax)	0.00338	.153	K_3FeCy_6 (from K_4FeCy_6)	0.0264	11.94

Organic Compounds.

Iodoform	0.00324	1.47	Chloral	0.0015	0.69
Anthraquinone	0.00428	1.94	Saccharine	0.00252	1.14
Vanillin	0.00208	0.94			

DISCUSSION

Vice-President HOWARD: This paper is now open for discussion.

Mr. LAIB: When Mr. Moore spoke of measuring the efficiency of the cell, he mentioned concentrated caustic in the cell possibly increasing the caustic content of the liquor flowing out of that cell, and therefore a possible wrong interpretation of the efficiency from that standpoint. Isn't it true that if he were to take a series of samples flowing from the cell, that that effect would be lessened at the time the next unit of extra strong caustic liquor was being stored up within the body of the cell itself; in other words, that you would average the effect?

Mr. MOORE: Mr. Chairman, in reply to that I would say that that was in the pages which I skipped in shortening the paper. That is all stated in the manuscript. In a long time test that will be largely nullified, and it takes a long time to test the result. You would never think of taking a boiler test on half an hour's time. Nevertheless you cannot test 500 cells for a longer period of time. You can test them every three months in order to get a general idea of how the cell is running and where the general result is the same you may have a few individual cells which will dam up and at times show a varying result, and sometimes the dam dissolves out so that you would get a higher efficiency. But the results show that the average is the efficiency of the plant, and it is better to give the results as a whole than to cut out some that you think are too high or too low. Probably of 500 cells only four or five would show over 100 per cent efficiency, while four or five others will show an efficiency less than the actual.

Mr. H. E. BATSFORD: I would like to ask what is the effect on the efficiency when you have to remove the contents of the cells.

Mr. MOORE: If you leave the cell full of brine, when you start the cell up you will have brine in the cathode compartment. You will find you have a lower efficiency than you ought to have because you are accumulating caustic and taking out brine. But if you let that run long enough for the dissolution to take place, then the efficiency will improve somewhat. In fact, in some plants, they regularly shut their cells down once in so often and wash the cells out with water, and the average efficiency of the Dillon-Collins plant for a year is between 95½ and 100 per cent. The curves which I have

presented show that both the current efficiency and the decomposition efficiency increase with the washing out of the cells.

Mr. A. H. Hooker: I have listened with great interest to the paper presented by Mr. Moore and feel it desirable that some of the points should be discussed. However, my own paper which is to follow nearly parallels his on some points; for that I would suggest postponing discussion until both papers are before the Meeting. Even then discussion of real value can hardly be presented except by a real study of the two papers.

Mr. Moore: Mr. President, I think that Mr. Hooker's paper will cover a good many of these points in a different way, and I think that it would be well for Mr. Hooker's paper to be presented, and then let the discussion proceed. I saw a part of his paper in New York after my paper was written. He puts some things in a different way, and his presentation may be more illuminating, at least I think it is. It will save duplicating energy.

THE CYLINDRICAL ELECTROLYTIC CELL

By L. D. VORCE

Read at the Montreal, meeting, June 28, 1920

THERE have appeared in the Journals, in the last few months, interesting articles on electrolytic cells, but with one exception, they have all been descriptive of the rectangular or box-shaped type. It has occurred to the writer that it might be equally interesting to outline in comparison, the so-called vertical cylindrical type, which is not so well known, principally for the reason that it has not been as widely advertised.

As the writer is largely responsible for the development and successful operation of a number of cell plants using this type of cell, he may be pardoned for having a paternal pride, as well as a well-founded belief in the efficiency of this type of electrolytic apparatus. Aside from the earlier work of Hargreaves, the beginning of the present development followed a commercial failure of one of the mercury cells.

In the first part of the last decade, an attempt was made to operate an electrolytic plant using the mercury cell patented by G. and G. W. Bell. To move the mercury from one compartment to the other, gas pressure was attempted. After a thorough trial it was found to be a failure, and was abandoned. Mr. A. E. Gibbs proposed, as a substitute, the use of a diaphragm cell. The original model, which was submitted was approximately four inches in diameter, and a foot high. The cathode consisted of ordinary perforated metal rolled into cylindrical shape with an asbestos diaphragm within, and graphite rod anode. The cathode was submerged, and the contention of the proponent at that time was that a diaphragm cell operating at 70% current efficiency, and 4 volts would be a commercial success, and could compete with the Castner Mercury cell with its high first cost and upkeep.

The hiatus between this experimental affair, and a commercially successful cell is rather considerable. One is reminded of Jasper Whiting's statement before the International Congress of Applied Chemistry in New York that "In my opinion the original idea is seldom worth more than ten per cent or even five per cent of the finished process."*

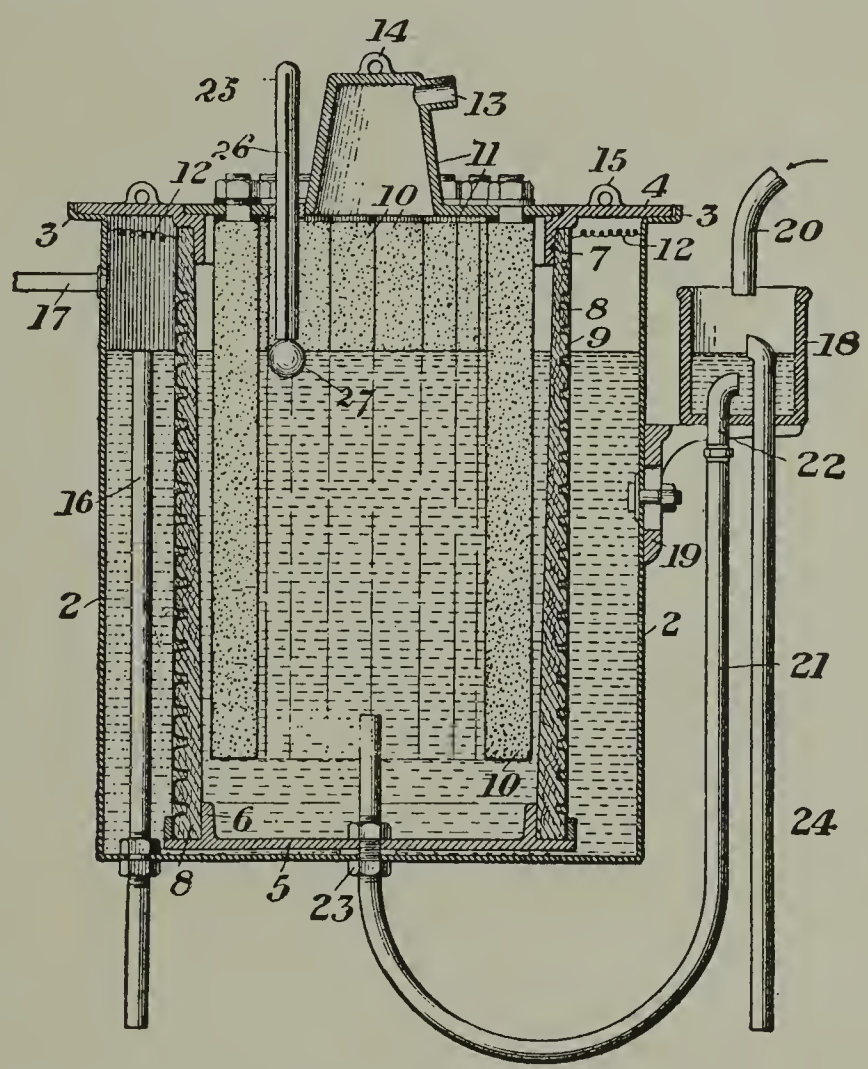
The attempt to multiply the dimensions of this experimental cell in three directions resulted in building one approximately four feet high, using as large a graphite cylinder for anode as could be secured. This was approximately ten inches in diameter, with a graphite plug screwed into the top for connection. The diaphragm was asbestos paper and cloth. It was evident that considerable deviation from the original idea was necessary to produce a satisfactory cell. The third cell was a considerable departure from the first and second, and resulted in a design which was a decided improvement and several of its features have survived in the cells as now used. Instead of one large carbon cylinder anode, several pieces of graphite, 2″×2″×36″ were used. For cathode the indented, or chisel slot opening perforated metal was used, the corrugations appearing inside later constituting the basis for patent claims. It is claimed that the use of this feature was accidental. However, it was found to give good results, and was retained in some of the plants, although it was conceded that ordinary perforations were just as efficient. The bottom and top rings upon which the cathode and diaphragm were built were of cast iron, covered with hard rubber as was also the dome, or cover, carrying the anode sticks which depended therefrom. An adjustable feed cup, with overflow for supplying brine and maintaining a constant head was attached to the side of the cell.

About this time it was discovered that in operating a caustic cell, the presence of liquor in the cathode chamber was unnecessary, and, in fact, a detriment as much better efficiency could be maintained by leaving the outside of the cathode unsubmerged. The credit for this discovery is in dispute and it is not within the province of this paper to discuss the priority since at the present time all claims covering that feature have expired. This cell is fairly well shown, in Patent No. 874064 of Dec. 17, 1907. This cell was started December 22, 1904, and ten were in operation in May 1905, when the writer took charge of the plant, and the development of the cell and process.

Between 1905 and the present time a great deal of study and ex-

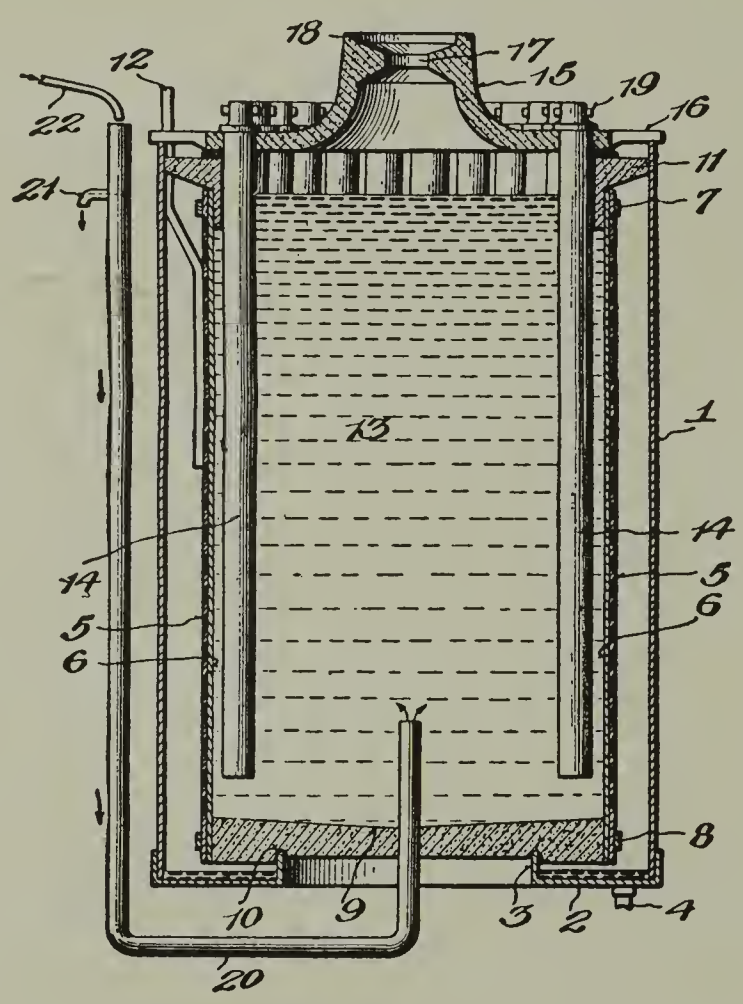
* (Vol. 21, Report of 8th Inst. Cong. of Appl'd. Chem.)

perimental work has been devoted to improvements in the details so that the circular cylindrical cell now presents a materially different aspect from that first shown. It is not necessary here to go at length into the details of the changes which were tried from time to time. The main idea was to preserve essential features but build as simply, economically and substantially as possible, avoiding all moving parts, and maintaining an apparatus easy to build, repair and operate, replacing metal wherever possible with the less corrodible material, concrete composition.



The embodiment of this development is illustrated in Patent No. 1,286,844. The design of the cell as now improved is much simplified, the complicated joints for the introduction of the brine supply at the bottom involving over a dozen parts have been reduced to a simple connection. Cement castings have taken the place of the rubber-covered cast iron members. The use of individual feed cups, entirely unnecessary, is eliminated, and the anode is supported independent of the cathode from the outside container, which relieves the cathode from any weight from that member and simplifies the construction.

Since the details of construction of the various cells have been published, it is allowable to make parallel comparison of their features for the convenience of those studying the process. In this connection, let it be at once understood that in making this comparison it is not with the idea of criticism of other cells, but rather to bring out for discussion such points as appeal to the judgment and experience of the men engaged in the practice of the art. It is to be expected that men working toward the same end, but differently situated as to place and experience, will travel the same general road,



but may differ materially in ideas, guided to a large extent by environment, materials available, and habit of thought.

With the present high cost of labor and material, one of the first points to be considered in a cell plant is floor space required. The cylindrical cell can be built in any desired size, within limits, but a standard has been adopted for a so-called 1000 ampere cell which is approximately 26″ in diameter, by about 40″ high. The rating of any such cell is purely arbitrary, as at a slightly increased voltage the current impressed upon a cell can be more than doubled as shown by Wheeler in a recent article. It is customary to set such cells in line on 30–32″ centers, with 40″ centers between the double lines, with a

result that the total working floor space required for this cell does not exceed fifteen square feet. This is much less than that for any rectangular cell. The cell room at the Edgewood Arsenal, housing 1776 Nelson cells, is 541′×82′, so that the working floor space for that cell of same current capacity is 25 square feet. The working floor space for the Allen-Moore cell, as calculated from data at the Dill & Collins plant, and at the Riordon Paper Company at Merittan, approximates 90 square feet for the so-called 1500 ampere cell, which would be about 60 square feet on a 1000 ampere basis. From data recently published of a German plant using the Billeter cell, the space required per 1000 ampere capacity is 70 square feet. The Hargreaves cell occupies about the same space. It is evident from these figures that in this respect the cylindrical cell can be housed in a much less expensive building. If these figures are translated into production per square foot, it is still more illuminating.

The Caustic production per day on the cylindrical cell is five pounds per square foot working space.

For the Nelson Cell 2.72 pounds per square foot (their guarantee) (Statement of efficiency of 92 per cent by Mr. Rollin).

For the Allen-Moore 1.21 pounds per square foot (their circular).

The production figures and space required are shown in the table below.

TABLE SHOWING CAPACITY OF CELLS

Cell.	Prod. per sq. ft. wrkng. spc.		Sq. ft. working space per ton of prod.	
	Caustic.	Chlorine.	Caustic.	Chlorine.
Cylindrical.....	5.00 #	4.43 #	400	450
Nelson.....	2.72 #	2.40 #	740	830
Allen-Moore.....	1.21 #	1.07 #	1650	1870

The circular design of cell lends itself to extreme simplicity in construction as well as giving the maximum effective operating surface to anode, cathode, etc. It also permits the construction of a cell with a minimum weight. In such a cell there are no massive parts of concrete, or metal to add weight without compensating advantages. A standard cylindrical cell will weigh not to exceed 600 to 650 lbs. The advertised weight of the Allen-Moore cell of 1500 amps. capacity is

2700 pounds. The light weight of the cylindrical cell is, in large part, obtained by the use of the asbestos-cement parts before mentioned. These are made in special cast iron moulds under pressure and can be made as desired at small expense. They stand the corrosive action very much better than the larger masses of concrete which require reinforcing, and being circular in form, are strong enough for the duty without being heavy. This lighter weight does not in any way detract from its stability, for the cylindrical shape of the cathode is best fitted to bear the strain of the anolyte without deformation to which it is liable on a flat surface. This is of importance in supporting the diaphragm free from ruptures.

In any cell it is essential to get the graphite anodes close to the cathode and diaphragm with as little resistance and consequently as few joints as possible. In this respect the cylindrical cell has a great advantage in that the design permits the use of graphite sticks which are as close to the diaphragm as in any cell, thus reducing the brine resistance to a minimum, and the anode is entirely without joints within the cell, connection with the source of power being made from the ends of the rods which pierce the cover of the anode compartment. Experience has shown that joints in the graphite within the cell not only call for greater labor and expense in assembling, but also add to the resistance of the cell through corrosion by the cell liquor. This can in a measure be minimized by treatment of the graphite to decrease its porosity but that, in turn, increases the resistance of the graphite to the passage of the current. With the arrangement of carbons as described, it is possible at all times to inspect and test the outside connection to locate any imperfect joint. It is palpably impossible to examine any joints where they are within the cell, except when it is shut down. The ability to build a cell without inside joints is considered very important.

Since Graphite is the most expensive item entering the construction of a cell, it must be used in as effective a manner as possible. To this end the shape which presents the greatest surface per unit volume is to be selected. In this feature the cylindrical cell again scores, using a graphite stick two inches square. There is thus a surface exposure of two square inches per cubic inch volume. In the Nelson cell with its 4×4 carbon this is reduced to 1 square inch per cubic inch volume. In the Allen-Moore cell, while the surface exposed to the cathode has one inch of surface per cubic inch of volume, these surface blocks are backed up by six inch cubes of graphite which in turn

have three inch rods, approximately three feet long, extending up through the cover for the external connection with the result that the total volume of graphite per cell is 6960 cubic inches for the 2880 square inches of surface exposed, or one square inch of exposed surface per 2.4 cubic inches in volume. In the Allen-Moore cell only the wide front surface, that is exposed to the cathode, is considered effective, while with the square anode sticks nearly all four sides are more or less active, as evidenced by the anodes of the Nelson cell which are found to corrode about equally on all four sides. In the cylindrical cell with its smaller size carbon, the action is also found to be upon all four surfaces.

The ratio of exposed anode surface to total volume in a cylindrical cell is 83.5 per cent. In the Nelson cell it is 75.5 per cent and in an Allen-Moore is 41.57 per cent. The current density per square inch of exposed surface would then be for the cylindrical cell $\frac{1000}{5760} = .0174$ amps.; Nelson cell $\frac{1000}{2912} = .0342$ amps.; Allen-Moore cell $\frac{1500}{2880} = .0522$ amps. If exception is taken to figuring all four sides of the carbon in the cylindrical cell and the back surface is considered non-effective, it still leaves $\frac{1000}{4320} = .0231$ amps. per square inch, which still is lower than that of the other cells.

In point of total weight of graphite used, the cylindrical cell requires 214 pounds; The Nelson 240 pounds; The Allen-Moore 440 pounds.

In the matter of efficiency of any cell, more depends upon outside conditions than upon the cell itself. That cell is yet to be built which is fool-proof. Many concerns have shifted from the use of one cell to another when the fault lay in the method of operation rather than in the cell proper. However, all things being equal, that cell is best which can be operated with the least trouble and expense, and the cell which is simplest to build, generally speaking, will be easiest to operate and maintain.

Since it is power which must be raised and paid for in a cell plant, it naturally follows that power efficiency is the end to which we should aim. A cell operating at 98 per cent current efficiency and 4.5 volts or a little above 50 per cent power efficiency is less economical than one at 90 per cent current efficiency and 4 volts. The cylindrical cell can be, and is, operated at a current efficiency approaching

98 per cent with a voltage not exceeding 3.6 volts and some cell plants run by the year at an average of 3.54 volts. With such low voltage, over 60 per cent power efficiency is easily maintained.

With the advancing cost of all material, freights and labor, the ability to operate cell plants locally where chlorine is required for bleaching makes it much more profitable for the paper maker to make his own bleach solutions when, where, and as wanted, than was formerly the case, and the moderate sized unit and flexibility of the cylindrical cell is felt to be a material factor in its favor.

DESCRIPTION AND VIEWS OF THE TOWNSEND CELLS AND THE NIAGARA FALLS PLANT OF THE HOOKER ELECTROCHEMICAL CO.

By A. H. HOOKER

Read at Montreal Meeting, June 28, 1920

In 1907 L. H. Baekeland described the general principles of the Townsend Cell and process of operation in the Journal of the Society of Chemical Industry and the Electrochemical and Metallurgical Industry. Since that time there has been a large development in the production of chlorine from these cells and some material modifications in design and operation have taken place. For that reason it seemed proper to bring before this symposium on electrolytic cells a brief description of the plant of the Hooker Electrochemical Company at Niagara Falls, where we are producing about 65 tons of caustic soda and 60 tons of chlorine daily from Townsend cells.

View No. 1 is a general view of the plant covering some 38 acres. In the left foreground will be seen the research laboratory; behind that, the chlorbenzol plant, where some 30 tons a day of chlorbenzol were made during the war for the French Government to be converted into dinitrophenol to modify their picric acid explosive; near that will be seen the plant for the manufacture of a very pure grade of muriatic acid, practically water white. The two larger buildings are the boiler plant, with a modern equipment of mechanically stoked boilers used to supply heat and steam for evaporation and process work and one of the evaporation houses containing vacuum pans and pots for finishing caustic. The two power-houses, five cell buildings, bleach chambers, brine purification tanks, machine and repair shops, office building, general laboratories, liquid chlorine and synthetic chemical units form the general group to the right of the picture, while in the distance can be seen the plant where we made picric acid for the Government from monochlorbenzol during the war.

This work all centers around the production and use of chlorine and caustic soda from the Townsend cells

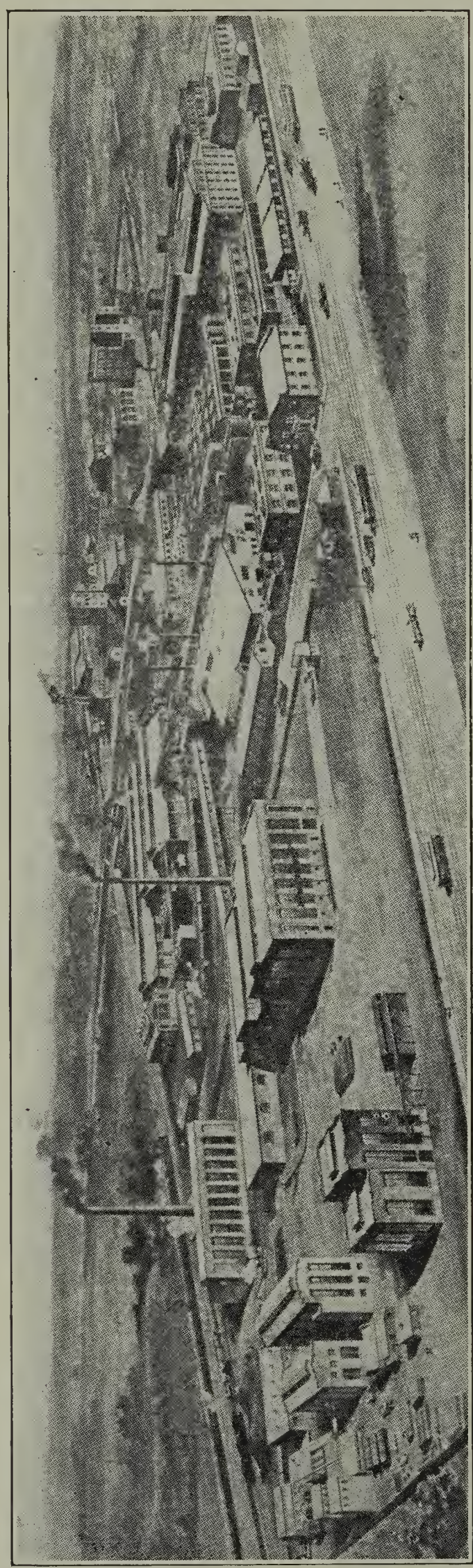


FIG. 1.—General View of Plant.

The power is received from the Niagara Falls Power Company as 3-phase, alternating current at 12,000 volts, and after passing through transformers and rotary converters, of which View No. 2 from one corner of our power house offers a typical example, is delivered to the cell circuits at some 260 volts and 4000–5000 amperes direct current.

We have several types of Townsend cell in operation, a small

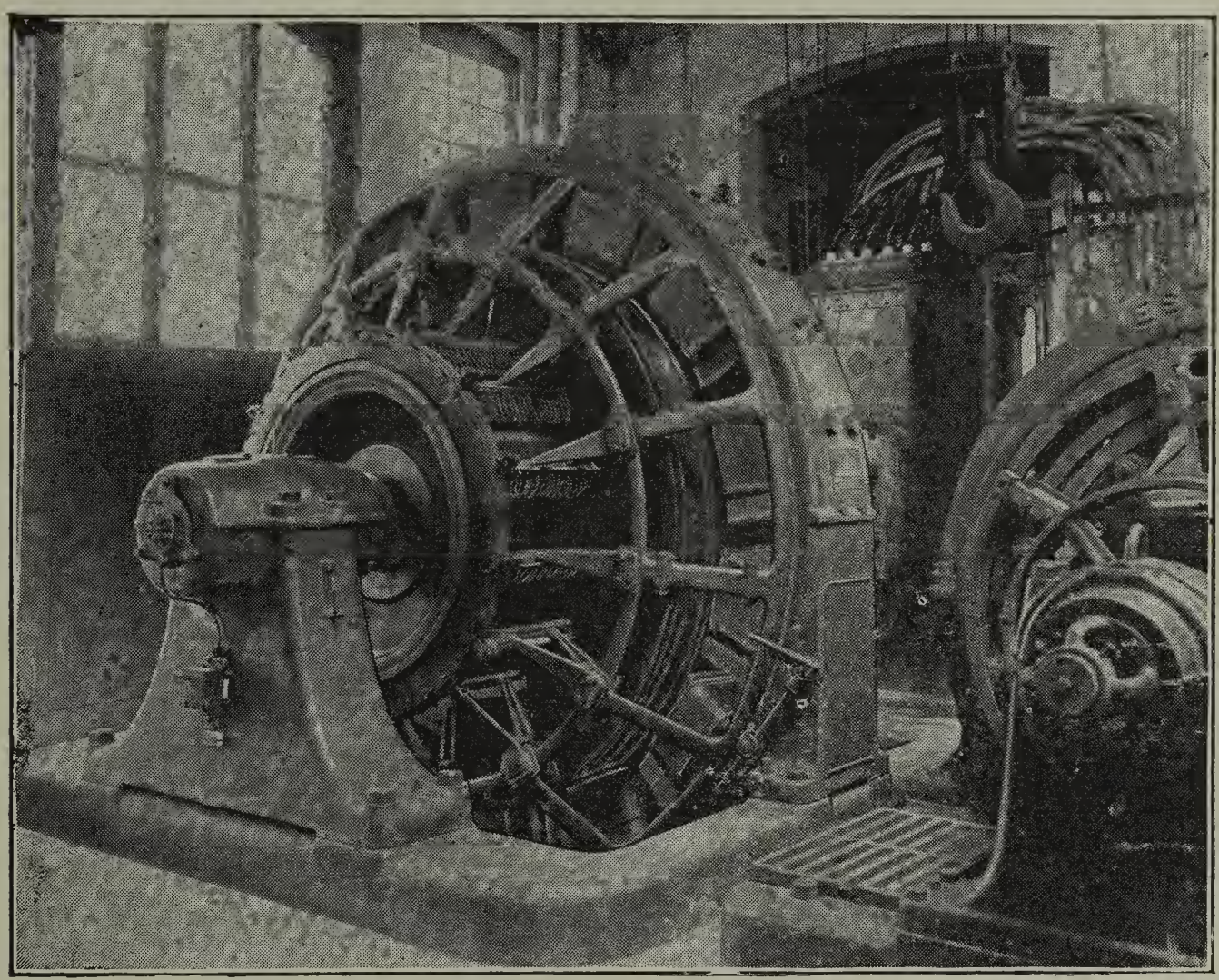


Fig. 2.—General Electric Rotary Converter, Showing Its Transformer in the Background.

circuit of the original 2500 ampere cells and some of the earlier 5000 ampere cells. However, View No. 3 will show one of our more recent cell bays, which consists entirely of 4000 ampere cells. In the building there are 120 cells each with a daily output of slightly over 300 pounds of caustic soda, or a total of 18 tons. View No. 4 is a more detailed view of one of these cells, which is of the long, low type of large capacity.

We find it expedient at Niagara Falls, with existing power costs to run at exceptionally high current densities, about 100 amperes per

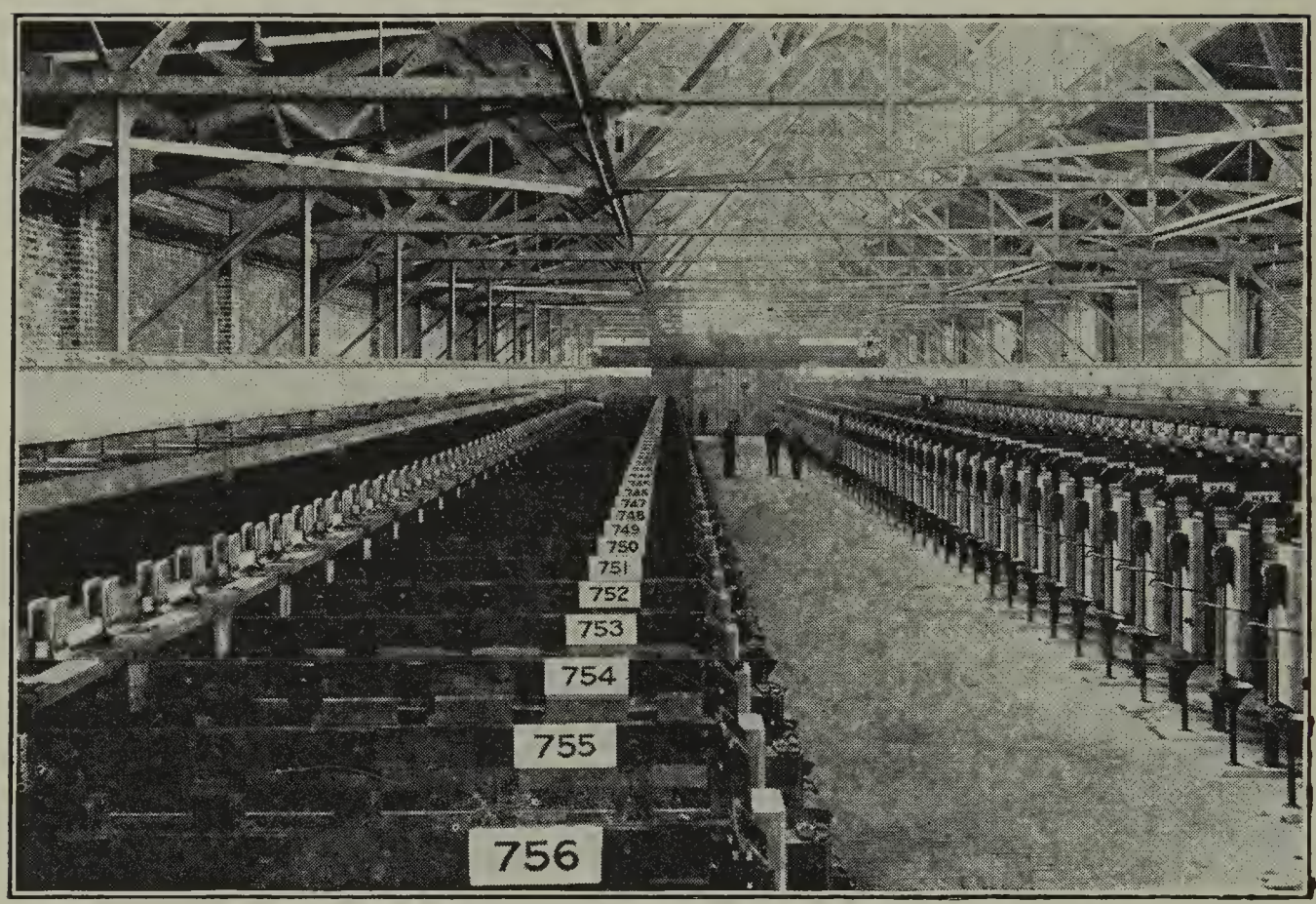


Fig. 3.—Cell House, Plant D.

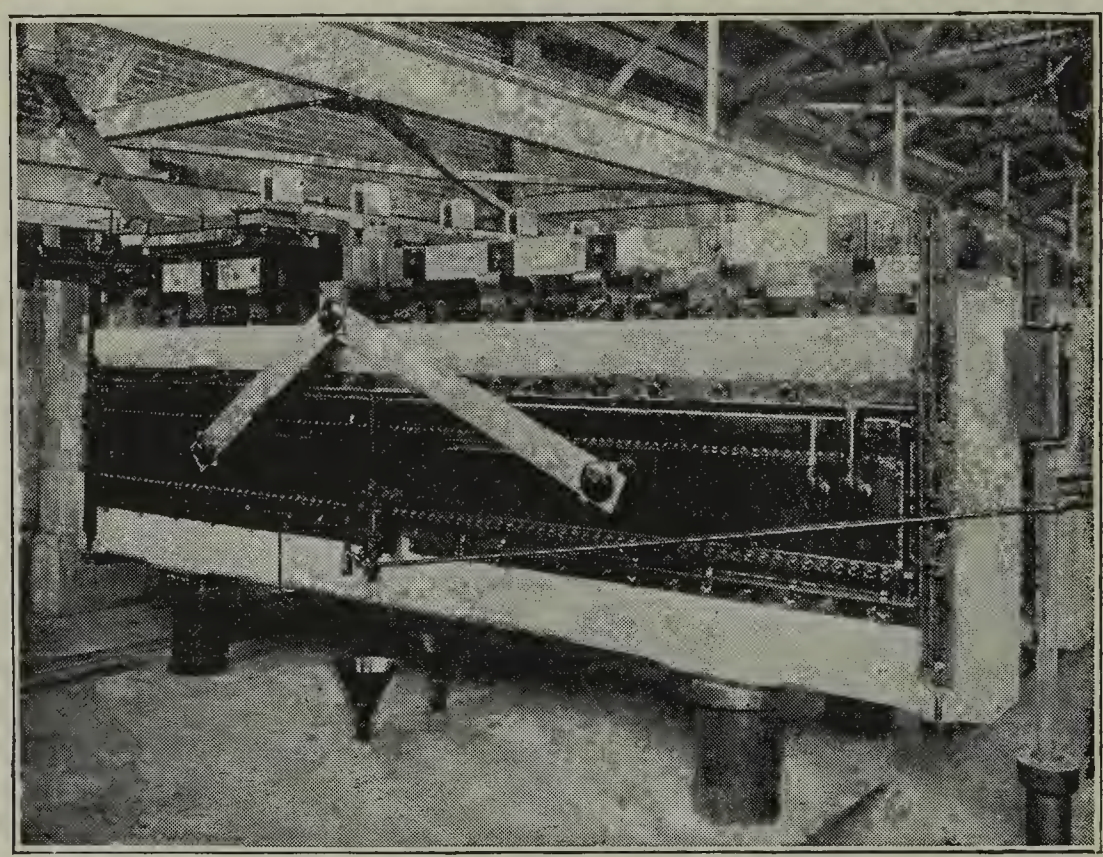


Fig. 4.—4000 Ampere Townsend Cell.

square foot of cathode, and hence use a little over 4 volts per cell during an average run, and an ampere or current efficiency of between 96 and 97%. Owing to the circulating system which we use to maintain saturation, as well as the novel use of oil in the cathode compartment, we are able to obtain this efficiency with a caustic strength considerably above 125 grams NaOH per liter.

Another interesting group of cells is shown in view No. 5, which we call the corrugated type of low cell. The previous design was

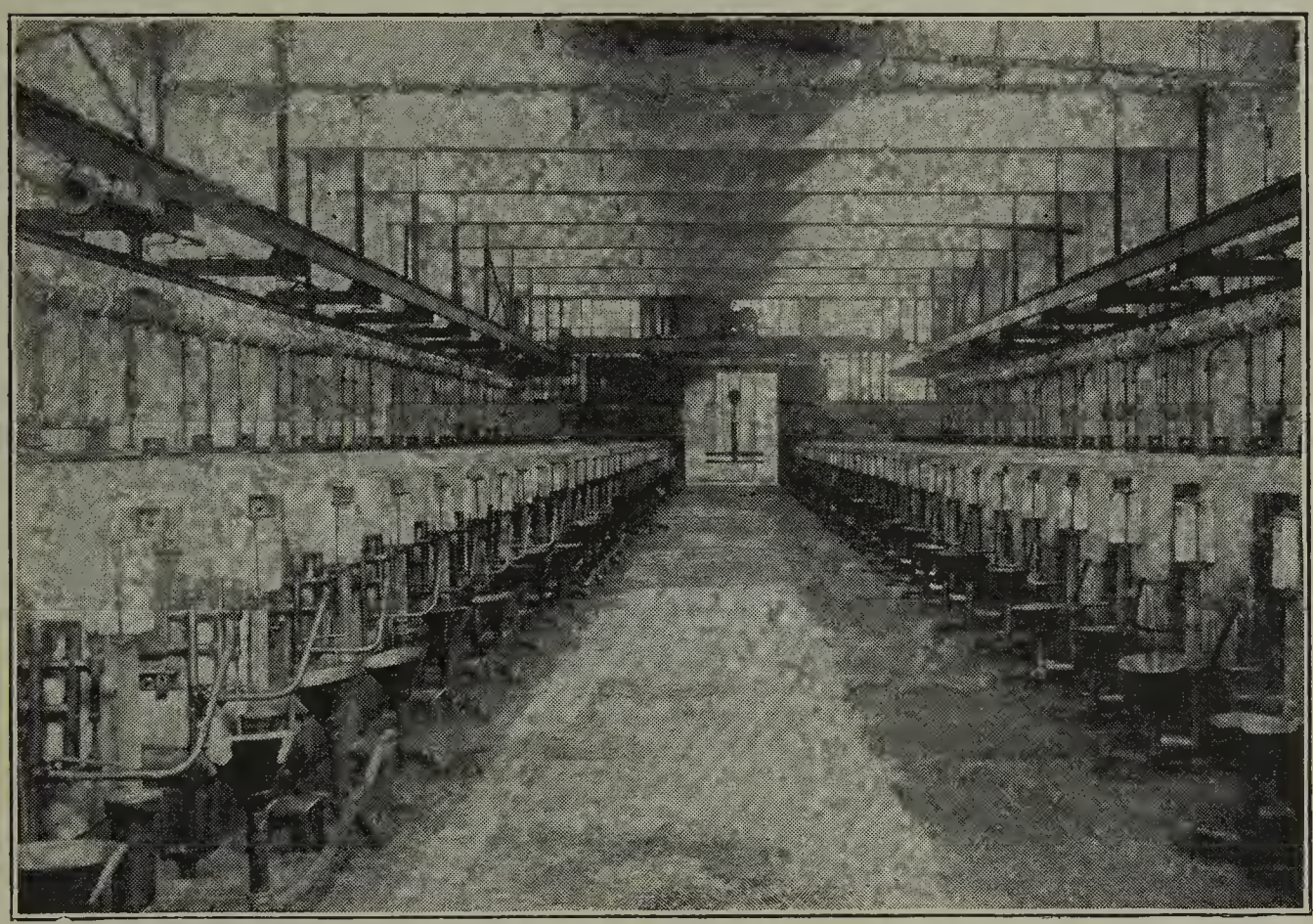


FIG. 5.—East Bay Cell House. View taken from south doorway looking north showing front view of Single Compartment Marsh Cells.

intended to give the maximum horizontal surface of cathode consistent with a large unit and the simplicity of the straight side plates. The cell shown in View No. 5 was designed to crimp this plate accordion fashion and thus permit a much greater horizontal surface for the escape of gas within the same ground area. This was intended to materially reduce the voltage of the cell at the same current density.

In this bay of 5000 ampere cells the result of lower voltage is fully accomplished and a natural saving is made both in the cost of installation and power. The design still requires some perfecting to work

out a perfect diaphragm control and simplicity of renewal repairs. Consequently, while power costs are low, the chemical efficiency is not quite as good, say 93 or 94%.

When it comes to a final monthly balance sheet with Niagara power costs the two groups run a very close commercial race, but there are other locations where a choice might clearly point to either one of the two types as best.

A study of the cathode liquors from these different types of cells has lead to some interesting results which I hope to bring out in the paper which follows.

CHEMICAL EFFICIENCY AND CONCENTRATION OF NaOH AND NaCl FROM TOWNSEND CELLS

SOME CHARACTERISTIC PROPERTIES OF SATURATED SOLUTIONS OF NaOH AND NaCl

By A. H. HOOKER

Read at Montreal Meeting, June 28, 1920

Solutions saturated with NaOH and NaCl at various temperatures form the products which we are constantly handling in dealing with the Cathode effluent from diaphragm cells used in the production of caustic soda. Winteler has given a very full table showing

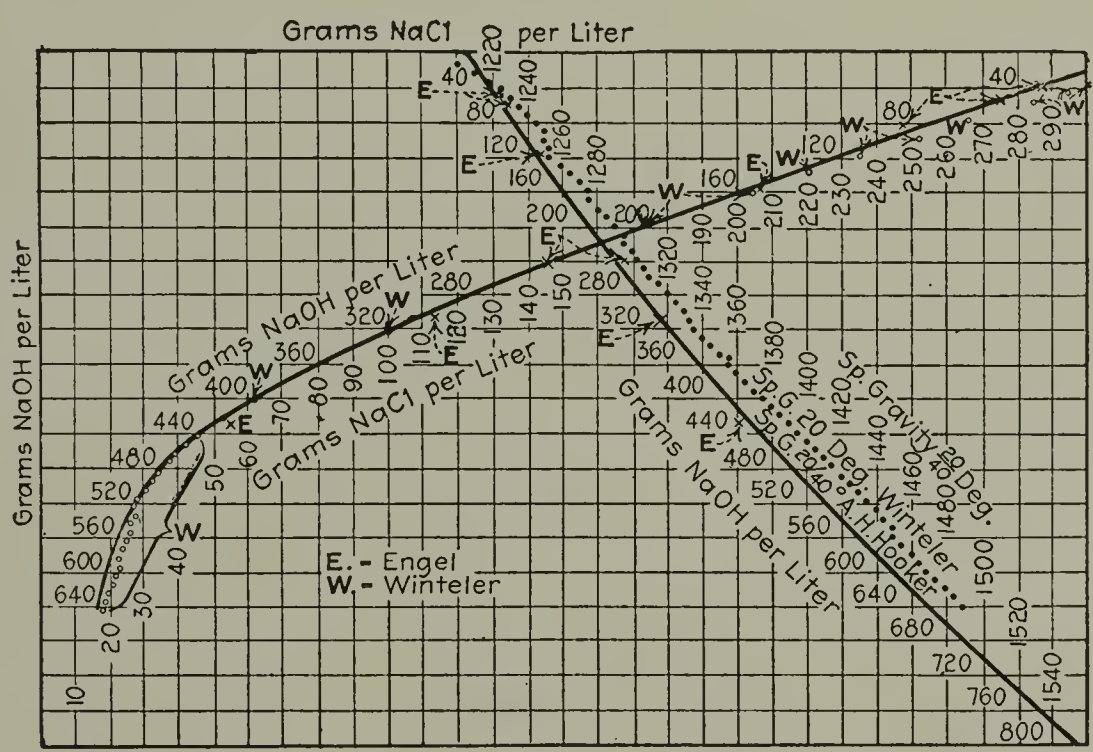


CHART 1.—Specific Gravity and Gram per Liter of Saturated NaCl–NaOH Solutions.

the grams per liter of NaOH and NaCl as well as specific gravity of the solutions saturated at 20° C. This table has been very freely used and is found in most of the literature, English, German and French, dealing with this subject. Engel has given a more limited series of observations not so generally used and based on determinations at 0° and 15° C.

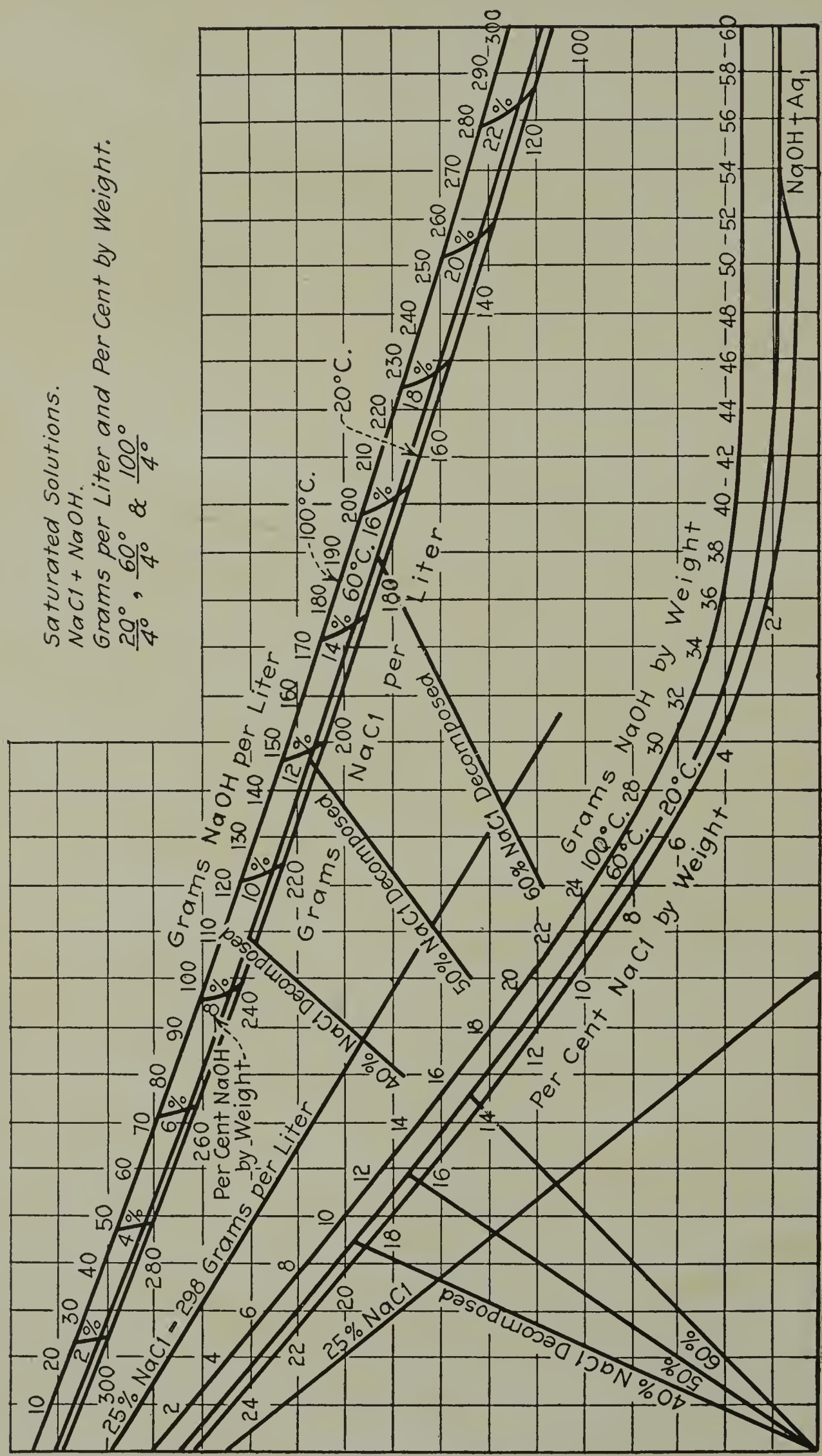


CHART 2.—Per Cent by Weight and Gram per Liter Saturated NaCl–NaOH Solutions.

About 1911 I had occasion to use the figures of Winteler reduced to per cent by weight by use of his specific gravity determinations, and, from these figures very slightly modified, prepared a number of rather complete saturation curves. Some of these I had intended to

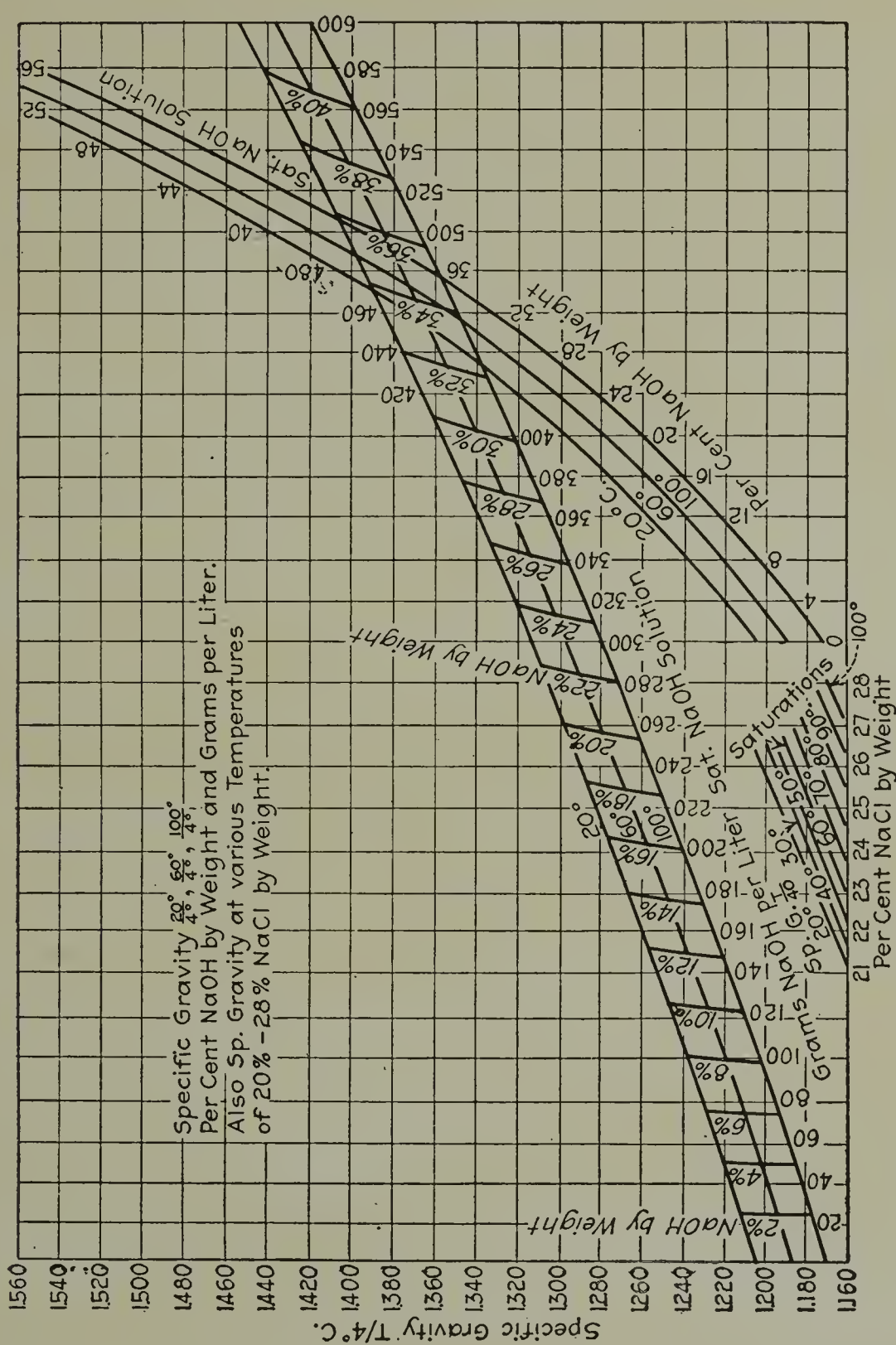


CHART 3.—Specific Gravities at 20°, 60° and 100° C. of NaCl–NaOH Solutions

use in this paper. However, experience has clearly shown that there were some material errors particularly in the specific gravity determinations of Winteler. I have, therefore, re-determined many of these figures and submit new figures which I hope with your crit-

icisms and corrections may form a substantial basis for future calculation. I might add that Winteler's figures considered only as grams NaOH and NaCl per liter agree closely to my own observations over the important range of the curve. The specific gravity figures offer the serious difficulty. Engel's figures, in general, agree much more closely in all regards, although the range is more limited. Chart No. 1 shows the essential differences and corrections which I have made and use in subsequent charts. Chart No. 2 shows per cent by weight and grams per liter of saturated solutions of NaOH and NaCl at 20°/4°—60/4°—100°/4°. Chart No. 3 shows the corresponding specific gravities for these solutions. Chart No. 4 shows

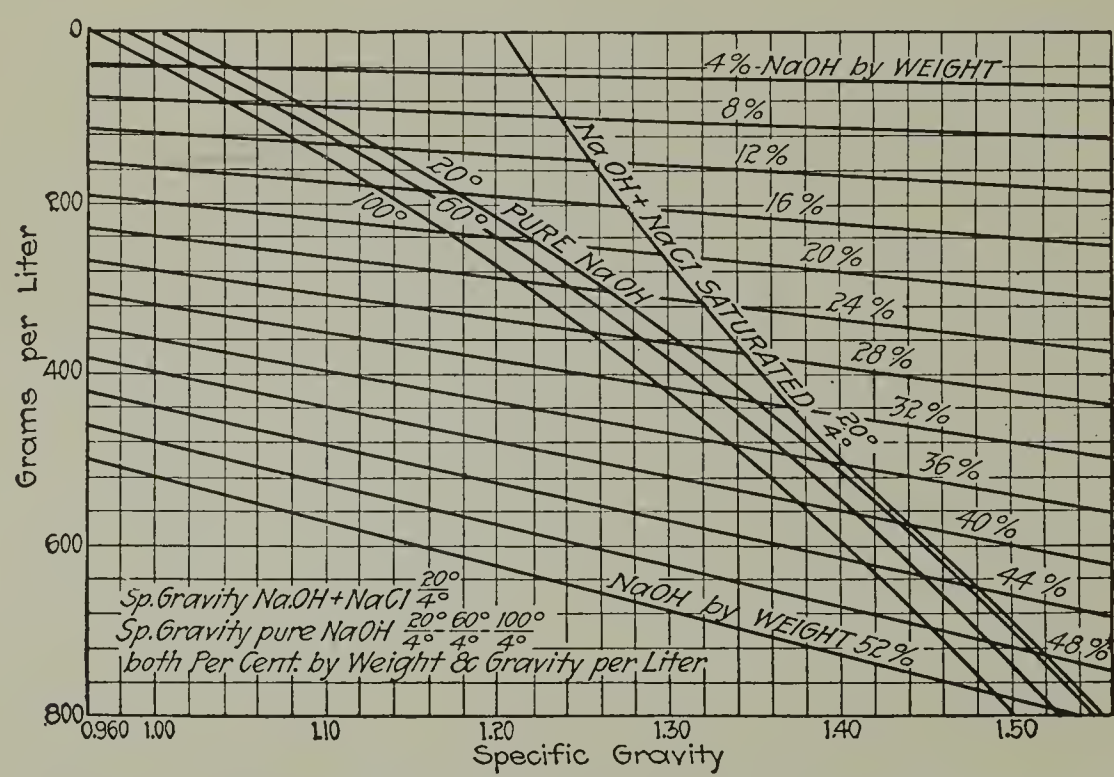


CHART 4.—Specific Gravities of NaOH and NaCl–NaOH Solutions.

specific gravity 20°/4°—60°/4°—100°/4° for pure NaOH solutions and, incidentally, for saturated NaOH and NaCl solutions at 20° C. This chart I have purposely ruled to bring out one feature which I found was not generally considered by our chemists in preparing curves and which I find quite useful. If a sheet of cross-section paper is prepared showing grams per liter on the lower margin and specific gravity on the side margin, say with a range in specific gravity from 1.000 to 1.500, obviously a line ruled from 100 grams per liter at 1.000 specific gravity connecting 150 grams per liter at 1.500 specific gravity will represent a 10% solution by weight at any intermediate specific gravity. A corresponding line from 120 grams per liter at 1.000 specific gravity to 180 grams per liter at 1.500

specific gravity will represent a 12% solution by weight at any intermediate specific gravity and to paper ruled in this way can be transferred figures either in per cent by weight or grams per liter at will, and both readings can be made from the same chart

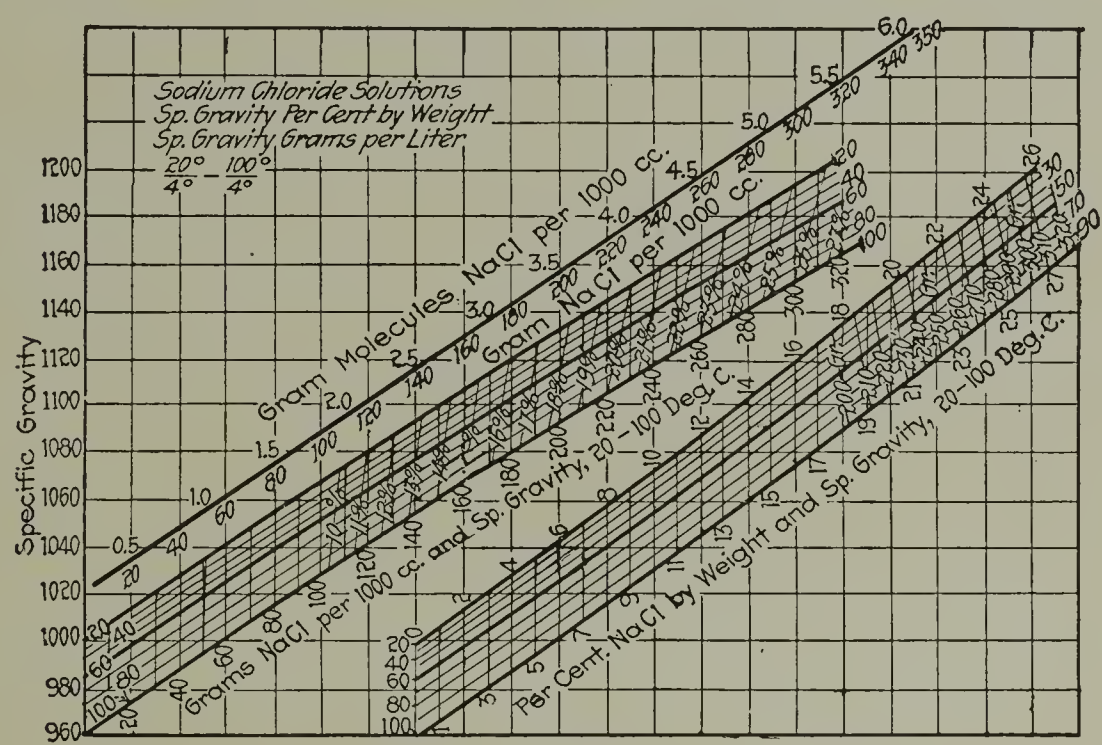


CHART 5.—Specific Gravities of NaCl Solutions.

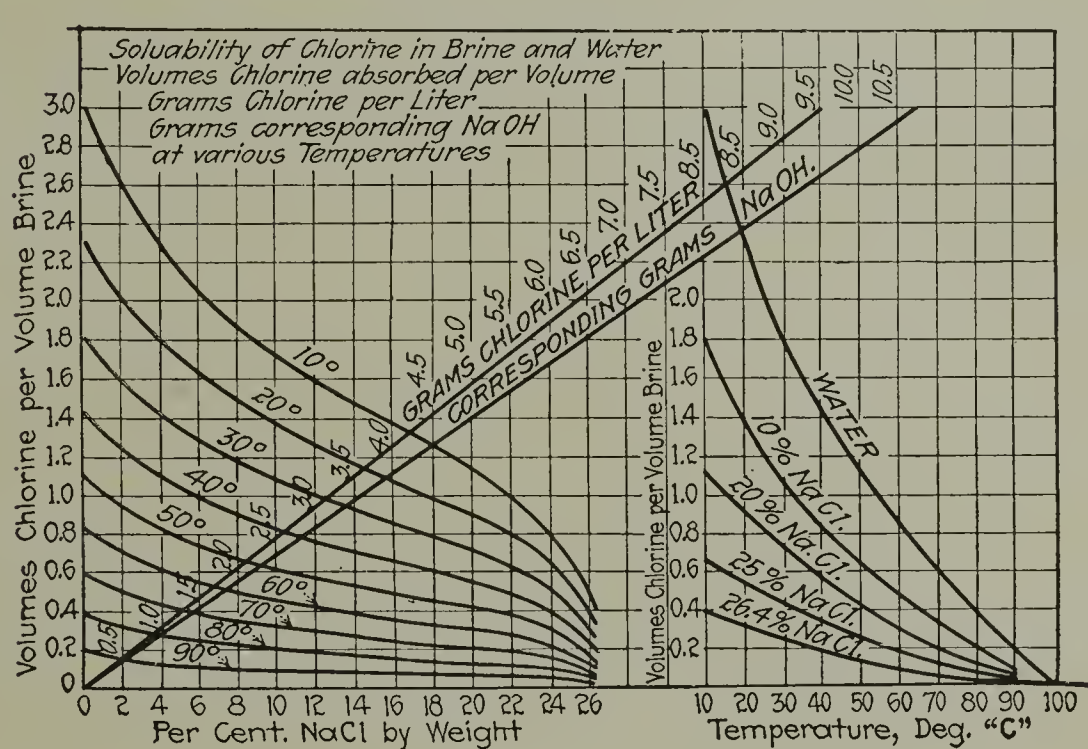


CHART 6.—Solubility of Chlorine in Brine and Water.

These figures for pure NaOH solutions at 20° agree closely with Lunge's tables at 15° with the necessary temperature correction, however, Lunge has published an extensive table showing the change

in specific gravity with temperature. I cannot make my own observations agree with Lunge's as to change in specific gravity with temperature, hence offer these figures at 60° and 100° for criticism and, I believe, correction of Lunge's figures.

Chart No. 5 gives the specific gravity and per cent by weight and grams NaCl per liter over a full range from 20°–100° C.

Chart No. 6 shows the solubility of chlorine in water and in brine of various strengths and a full range of temperatures. Also the solubility in grams of chlorine per liter and the corresponding grams NaOH which would be converted by this chlorine into hypochlorite in the cathode compartment of a cell. These first six charts are presented as the basis for those which are to follow.

If we consider in rather simple terms the reaction which takes place on electrolizing salt in a diaphragm cell, we can express it after the sodium has decomposed water to form hydrogen by the formula $NaCl+(X_1H_2O=NaOH+(X-1)H_2O+Cl+H$. In ordinary operations there is a certain ratio of salt decomposition which offers the greatest economy for a given cell—giving due consideration to the cost of power, coal, renewals, etc. This range is usually between 40% and 60% salt decomposition. Assuming for consideration an intermediate figure of 50% and the use of 25% brine by weight, also a formula which will express the brine depletion in the anode compartment without resorting to transport numbers, we have the following:

$$2NaCl + 19.5\,H_2O + (5H_2O) = NaOH + NaCl + 18.5\,H_2O + Cl + H + (5H_2O)$$

117	351	90	40	58.5	333	35.5	1	90
292.5	877.5	225	100	146.25	832.5	88.75	2.5	225

FEED BRINE

292.5 NaCl = 25% by Wt.
877.5 H_2O = 75% by Wt.

1170.0 = 981 cc. = 298 grams per liter.

CATHODE NaOH

100 NaOH = 9.27% by Wt. = 111.8 grams per liter
146.25 NaCl = 13.56% by Wt.
832.50 H_2O = 77.17% by Wt.

1078.75 = 894 cc.

Anode brine within the cell
292.5 NaCl = 20.96% by Wt.
1102.5 H_2O = 79.04% by Wt.

1395.0 = 243 grams per liter.

We can entirely disregard efficiency in this formula and express the result in terms of product and efficiency as the time or amperes needed to produce 100 grams of NaOH.

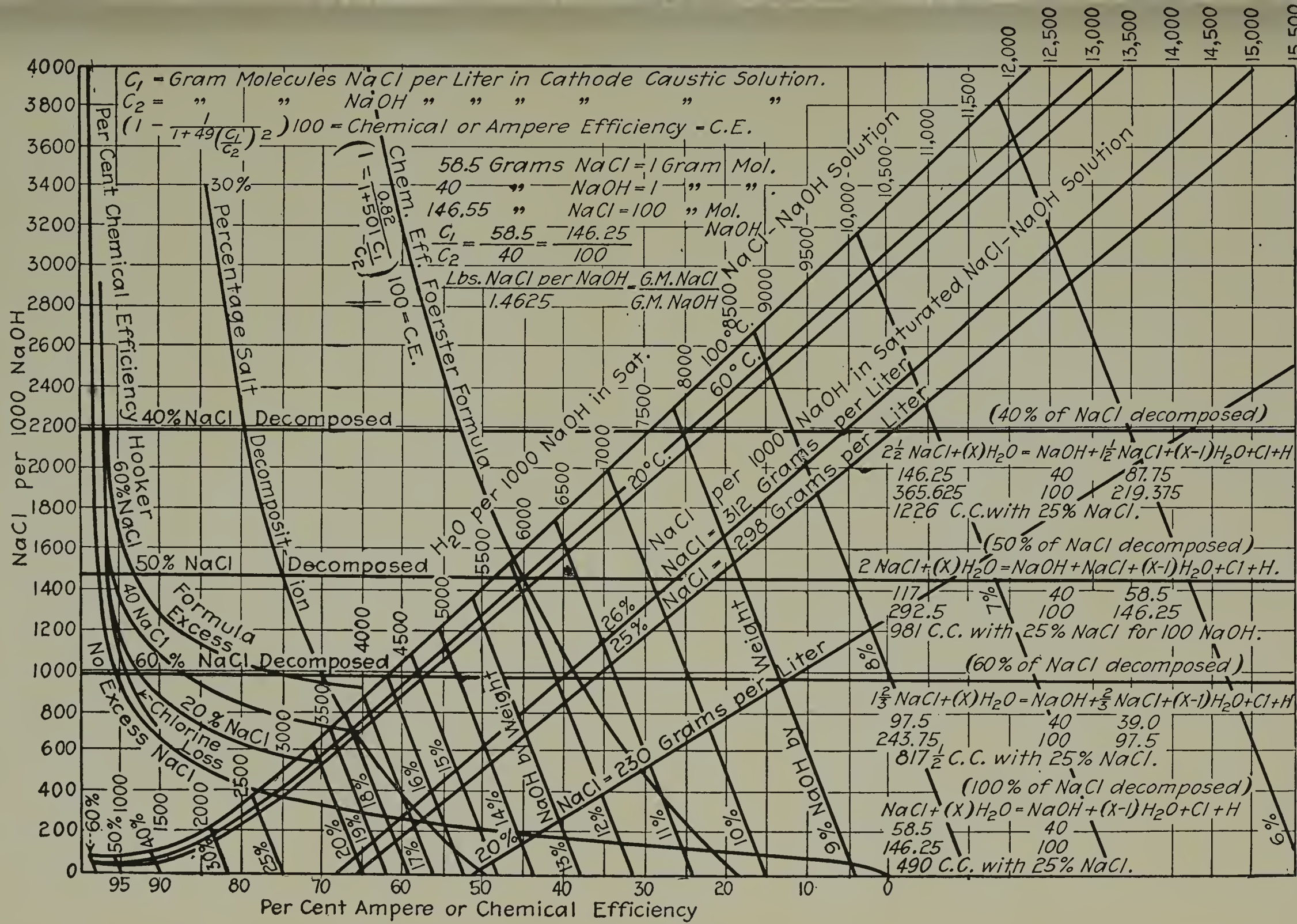


CHART 7.—Water and Salt Ratios to NaOH Chemical Efficiencies.

[To face page 66.]

Turning now to Chart No. 7 we have charted the results of 20%–25% and 26% solutions of NaCl by weight at any rate of decomposition in terms of H_2O and NaCl per 1000 HaOH which represent the simplest values for a direct commercial valuation of cathode liquors in terms of coal or evaporation costs.

Next on this same chart from our previous saturation curves are plotted saturated solutions of NaCl+NaOH at 20°–60°–100°. Now it is well known that the Townsend cell as operated at our Niagara Falls Plant uses an extensive circulating system both to remove impurities in the brine and therefore increase the life and efficiency of the diaphragm and to maintain the desired degree of saturation within the cell at all times. We can thus obtain a cathode solution that is fully saturated at 20°. In fact with a temperature of 60° within the cell, we can readily exceed this point, but care must be taken not to do this except to a slight degree, otherwise trouble results from salt deposits at various points.

Turning now to our Chart we find the following results:

50% decomposition	50% decomposition
25% brine	brine circulated and saturated
1000 NaOH	1000 NaOH
1462.5 NaCl	1462.5 NaCl
8325.0 H_2O	6250 H_2O

This difference then is 2,075 pounds water per 1,000 pounds NaOH produced. Nor is this the only difference. We have seen that there was required 981 cc. of 25% brine to supply 292.5 grams of salt for 100 grams of NaOH in the original equation while with the saturating system only 750 cc. of brine would be supplied and the remaining salt would be added in the solid state to the saturating vault to be dissolved in the slightly depleted anode circulation.

Now turning to our Chart relative to the solubility of chlorine in brine, we find that 1000 cc. of 21% brine will dissolve 280 cc. chlorine (760 mm. 0°) = .8876 grams. This, in turn, corresponds to 1.00 gram NaOH. Hence 981 cc. would carry chlorine = 0.981 grams NaOH to the cathode compartment, thus reducing the product or efficiency by practically 1%—(the greater the feed of brine, viz., the lower the decomposition with a given brine, the greater the loss). Also 1,000 cc. 25% brine will dissolve 170 cc. chlorine at 60° = .539 grams = .60 gram NaOH, hence 750 cc. = 0.45 gram lost NaOH = 0.45% drop in efficiency, hence we are better off by fully ½% in

efficiency by maintaining saturation. These chlorine losses are also shown on Chart No. 7 relative to efficiency.

There is another and much more vital factor in efficiency that this form of chart which I believe is rather unique, permits of bringing out, and which permits of a very rational comparison of different cell performances, a study of diaphragm and general structural difficulties.

It is well known that over the ordinary working range of commercial operations with the same feed brine, an increase in concentration of cathode caustic results in a decrease in efficiency, other conditions being equal (at extreme dilutions this curve reverses, owing to the solubility of chlorine in brine). I have sometimes used as an entirely empirical formula from observation $33\frac{1}{3}\%$ decomposition, viz., 292.5 NaCl per 100 NaOH, 98% ampere efficiency, 50% decomposition, viz., 146.25 NaCl per 100 NaOH 96% ampere efficiency, 60% decomposition, viz., 97.50 NaCl per 100 NaOH 88% ampere efficiency—this, however, contains two variables working in opposite directions, viz., increase in inefficiency, due to increase in salt ratio and decrease in efficiency due to increase in volume of brine with dissolved chlorine as a loss. Hence, I submit the following formula for chemical or ampere efficiency, with a perfect diaphragm and uniform percolation over its entire surface (this, of course is only an approachable ideal):

C_1 = gram molecules NaCl in effluent cathode caustic;

C_2 = gram molecules NaOH in effluent cathode caustic;

$$\left(1-\frac{1}{1\div 49\left(\frac{C_1}{C_2}\right)^2}\right)=100=\text{chemical efficiency.}$$

40% decomposition $60/40=c_1/c_2=3/2$ $(3/2)^2=9/4=2.25$ hence

$$\left(1-\frac{1}{1-49}\left(\frac{C_1}{C_2}\right)\right)100=99.1 \text{ C. E.}$$

50% decomposition $50/40=c_1/c_2=1/1(1/1)^2=1$ hence 98% C. E.
60% decomposition $40/60=c_1/c_2=2/3(2/3)^2=4/9$ hence 95.6% C. E.

We must calculate our loss of absorbed chlorine separately as previously shown by the volume and strength of brine within the

cell and the operating temperature. For example, an experimental cell operating at 20°–30° will have a much greater chlorine loss than a large cell maintained at a high temperature.

Taking all these factors into consideration, our curves indicate an ideal efficiency of say 95% with 60% decomposition (a result I never have obtained) 97%–97.5% at 50% decomposition and 97.5%–98% at 40% decomposition. The intermediate curves point to commercial results of various types and imply a mixed decomposition at various parts of the cell.

If we assume that for 100 grams of NaOH produced in unit time, we feed 292.5 grams of NaCl—146.25 grams are decomposed and 146.25 grams remain with the effluent caustic at 50% decomposition, this should result 97–97.5% ampere efficiency according to whether we figure on a 25% brine feed or saturation of the cathode caustic Now suppose we find only 95% ampere efficiency corresponding to 60% decomposition or 97.5 pounds NaCl per 100 NaOH, this means that 146.25 − 97.5 = 48.75 NaCl per 100 NaOH has passed through the diaphragm to the cathode caustic performing no really useful purpose this would mean 194 pounds of 25% excess brine to handle for every 100 pounds NaOH produced. There are many commercial cases far worse than this that could be cited. Probably no original diaphragm is at its best until a true "Schmutz Decke," as the water filtration people say, is formed and certainly it makes a material difference whether there is a varied flow and consequently varied decomposition at different heights of the same cell. I offer these provisional curves as a new basis for study in cell efficiency and performance.

Another useful function of Chart No. 7 will, I think, appeal to Mr. Hugh K. Moore. I refer particularly to its use in connection with caustic evaporator problems such as he so ably described at the St. Louis meeting in 1917. This chart permits of following directly any caustic solution at any temperature from start to finish through the vacuum pans if we start with the product of 50% decomposition, and 25% brine having a composition of 1000 NaOH, 1462 NaCl, 8325 H_2O.

We concentrate until we reach 1000 NaOH, 1462 NaCl, 5600 H_2O, loss 2725 pounds H_2O, before any salt separates out after this there is a constant removal of salt and water in the proportion of about 2800 pounds water per 1000 pounds salt until we reach about 30% NaOH by weight. Here the rate of salt to water changes, although we now

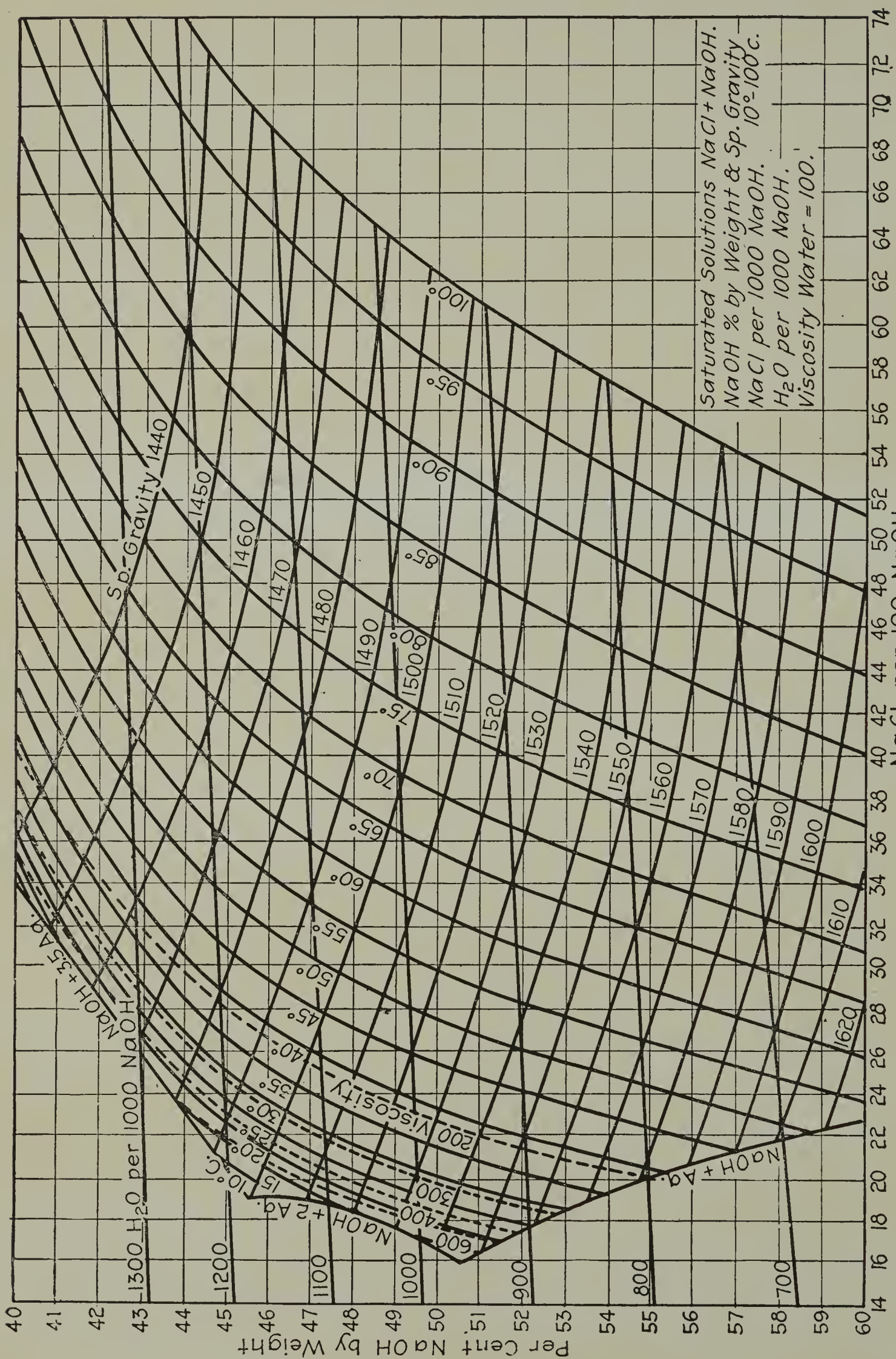


CHART 8.—Concentration of NaCl in NaOH Solution.

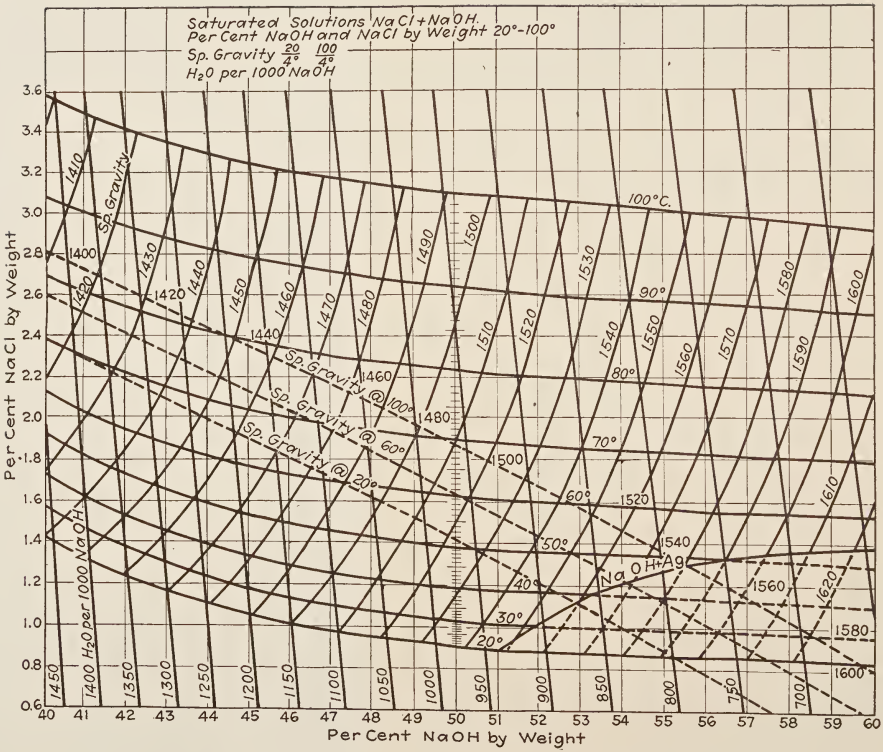


CHART 9.—Percent of NaCl and NaOH Having Evaporation.

[*To face page 70.*]

have only 200 pounds salt left from our original 1462 pounds per 1000 NaOH.

At about 50% concentration we have approximately 60 pounds salt left for 1000 NaOH and this can not be materially reduced (as will be seen by the abrupt turn of the curve) by farther concentration in the evaporators—however commercial grades of finished caustic require a material reduction beyond this point. A glance at the curve shows that nearly two-thirds of the salt present at this stage at 100° can be removed by cooling to 20°. As this is a somewhat critical operation, it becomes desirable to magnify the small fraction of our curve between 40% NaOH and 60% NaOH. I prepared an interesting curve on this order in 1911. I believe Mr. Barton of the Berlin Mills has a copy which I gave him. I am not sure that any other copies were given out. I know that Mr. Mantius of the Zaremba Company used one of our copies on our work—this chart was quite complete as you will see by the blue print which I am circulating, and contained in addition to the figures on Chart No. 9 which I am showing the resulting analysis from finishing certain grades of caustic liquor. I have purposely left these figures from the present chart which is materially corrected to correspond to more recent results which have gradually accumulated showing some variation from the original. While it is true that lines can be introduced showing the finished grade, these will depend upon individual plant practice, partly as regards sulphate and carbonate, but particularly as to chlorate in the final liquors, hence are not constant. The figures for viscosity I prefer to use not as I did on the old chart, but in a final chart which I will introduce.

This Chart No. 9 shows per cent NaOH by weight and per cent NaCl by weight, also specific gravity and pounds water per pound NaCl. It should be borne in mind that in cooling a saturated solution of salt and caustic that the caustic water ratio remains constant while the salt ratio varies, hence, if we start at say 100° with 1000 NaOH or 51% NaOH.

900 H_2O..... 3.1% NaCl

and cool to say 40° we will still have 1000 NaOH but with 52% NaOH

900 H_2O..... 1.18% NaCl

While this chart gives all the necessary information, I much prefer to use this information in the form shown in Chart No. 8 which, I

believe, is quite original in its arrangement, yet makes a most convenient form for arriving at the desired results in finishing caustic. If we start with a 51% solution of caustic this at 100° will have a specific gravity of 1.503 and 1000 pounds NaOH 900 pounds H_2O 62 pounds NaCl cooling to 40° C. we have practically 52% caustic by weight. 1000 pounds NaOH 900 pounds H_2O 22 pounds NaCl specific gravity 1550 our viscosity which plays a very important part in the final time of settling of salt is now practically 200 compared to water—as 100—by still further cooling to 25° C. we have a specific gravity of 1560 a solution containing 1000 NaOH 900 H_2O 18 NaCl but our viscosity has reached nearly 400, making it practically impossible to settle out this last 4 pounds of salt. Also we are at the point of freezing or solidification for part of our solution, hence, have passed the limits with this particular solution.

It is quite obvious that clear across this chart with 20–25 or 30 pounds of salt the same grade of finished caustic will result and could be plotted out—to this salt must be added the salt from decomposing chlorates which varies with different plant operations. We have now passed from a cell liquor containing:

1000 pounds NaOH to a solution containing 1000 NaOH
8325 pounds H_2O to a solution containing 900 H_2O
1462 pounds NaCl to a solution containing 22 NaCl

And I think can leave the final finishing in the pots for another story.

20°

Per Cent NaOH by Wt.	Per Cent NaCl by Wt.	Per Cent H_2O by Wt.	Sp. Gr. 20°/4°.	Grams NaOH per Liter.	Grams NaCl per Liter.	Grams H_2O per Liter.	NaCl per 100 NaOH.	H_2O per 100 NaOH.
0	26.4	73.6	1204	.....	313	886		
2	24.73	73.27	1211.5	24.23	299.6	887.67	1236.48	3663.22
4	23.05	72.95	1219.5	48.78	281.09	889.63	576.24	1823.76
6	21.	72.7	1228	73.64	261.56	892.76	354.96	1211.67
8	19.6	72.4	1237	98.96	242.45	895.59	244.99	904.80
10	18.05	71.95	1245.5	124.55	224.8	896.1	179.7	719.5
12	16.5	71.5	1255	150.6	207.08	897.3	137.5	595.8
14	14.98	71.02	1265	177.1	189.5	898.4	107	507.3
16	13.45	70.55	1275	204	171.5	899.5	84.1	440.9
18	11.9	70.1	1285.5	231.39	152.97	901.14	66.7	393.7
20	10.45	69.55	1296.	259.2	135.4	901.4	52.2	347.7
22	9.05	68.95	1307.25	287.60	118.31	901.1	41.1	313.3
24	7.75	68.25	1318.5	316.44	102.2	899.9	32.3	286.2
26	6.5	67.5	1331.	346.06	86.5	898.4	25.	259.6
28	5.3	66.7	1343.5	376.18	76.5	895.1	19.0	237.9
30	4.29	65.71	1358.25	407.48	58.27	892.5	14.3	219.
32	3.27	64.73	1373.	439.36	44.9	888.74	10.2	202.1
34	2.6	63.4	1389.	472.26	36.1	880.64	7.6	186.5
36	2.07	61.93	1405.	505.80	29.1	870.1	5.7	172.2
38	1.75	60.25	1422.5	540.5	24.9	857.1	4.6	158.5
40	1.44	58.56	1440.	576.	20.7	843.3	3.6	146.5
42	1.26	56.74	1460.	613.2	18.40	828.4	3.0	135.
44	1.09	54.91	1480.	651.2	16.1	812.7	2.4	124.8
46	1.01	52.99	1499.5	689.8	15.1	794.6	2.1	115.2
48	0.94	51.06	1519.	731.1	14.3	773.6	1.9	105.8
50	0.91	49.09	1538.	769.	13.9	755.1	1.8	98.2
52	0.89	47.11	1559.	810.68	13.9	734.42	1.7	90.59
54	0.87	45.13	1580.5	853.47	13.9	713.13	1.6	82.38
56	0.86	43.14	1603.	897.68	13.9	691.42	1.55	77.01
58	0.85	41.15	1625.5	942.79	13.9	668.81	1.47	70.94
60	0.84	39.16	1649.	989.4	13.9	645.7	1.40	65.26

60°

Per Cent NaOH by Wt.	Per Cent NaCl by Wt.	Per Cent H_2O by Wt.	Sp. Gr. 60°/	Grams NaOH per Liter.	Grams NaCl per Liter.	Grams H_2O per Liter.	NaCl per 100 NaOH.	H_2O per 100 NaOH.
0	27.0	73.	1187.	.....	320.49	866.51		
2	25.3	72.7	1194.75	23.90	301.26	869.59	1260.50	3635.0
4	23.61	72.39	1202.5	48.10	283.91	870.49	590.24	1809.75
6	21.94	72.06	1210.5	72.63	265.58	871.29	365.66	1201.
8	20.27	71.73	1219.	97.52	247.09	874.39	253.37	896.62
10	18.7	71.3	1228.	122.80	229.64	875.56	187.00	712.91
12	17.13	70.87	1237.	148.44	211.90	876.66	142.75	590.59
14	15.61	70.39	1246.5	174.51	194.58	877.41	111.49	503.07
16	14.09	69.91	1256.	200.96	176.97	878.07	88.06	437.43
18	12.6	69.4	1266.	227.88	159.52	878.6	70.0	385.77
20	11.11	68.89	1277.	255.4	141.87	879.73	55.54	344.45
22	9.76	68.24	1287.5	283.25	124.46	879.79	44.4	310.60
24	8.42	67.58	1299.	311.76	109.37	877.87	35.08	281.58
26	7.20	66.88	1312.	341.12	94.46	876.42	27.39	256.89
28	5.98	66.02	1325.	372.	79.24	873.76	21.30	234.67
30	4.97	65.03	1338	401.4	66.5	870.1	16.56	217.26
32	3.97	64.03	1352.5	432.8	53.69	866.01	12.40	200.09
34	3.37	62.63	1367.5	464.95	46.08	856.47	9.91	184.20
36	2.77	61.23	1384.	498.24	38.34	847.42	7.51	170.08
38	2.46	59.54	1401.	532.38	34.46	834.16	6.47	156.68
40	2.15	57.85	1419.	567.60	30.51	820.89	5.37	144.45
42	1.98	56.02	1437.5	603.75	28.46	805.29	4.71	133.38
44	1.81	54.19	1457.	641.08	26.37	789.55	4.11	123.16
46	1.74	52.26	1476.25	679.07	25.69	771.49	3.77	113.60
48	1.67	50.33	1496.	718.08	24.98	752.94	3.48	104.85
50	1.64	48.36	1516.	758.	24.86	733.14	3.28	96.72
52	1.61	46.39	1536.25	798.85	24.86	712.54	3.11	89.19
54	1.59	44.41	1557.	839.78	24.86	692.36	2.96	82.44
56	1.57	42.43	1578.5	883.96	24.86	669.68	2.81	75.75
58	1.55	40.45	1601.	928.58	24.86	647.56	2.66	69.73
60	1.53	38.47	1624.5	974.70	24.86	614.94	2.55	63.11

100°

Per Cent NaOH by Wt.	Per Cent NaCl by Wt.	Per Cent H_2O by Wt.	Sp. Gr. 100°.	Grams NaOH per Liter.	Grams NaCl per Liter.	Grams H_2O per Liter.	NaCl per 100 NaOH.	H_2O per 100 NaOH.
0	28.2	71.8	1170.	.....	329.94	840.16		
2	26.54	71.46	1177.5	23.55	312.50	841.45	1326.97	3572.82
4	24.88	71.12	1185.	47.40	293.73	843.87	622.0	1778.00
6	23.20	70.80	1193.	71.58	276.78	844.64	386.66	1180.00
8	21.52	70.48	1201.5	96.12	258.56	846.82	268.99	881.00
10	19.96	70.04	1210.5	121.05	241.62	847.83	199.59	700.39
12	18.4	69.6	1219.5	146.34	224.39	848.77	154.85	580.0
14	16.89	69.11	1229.	172.06	207.68	849.26	120.70	493.50
16	15.38	68.62	1238.5	198.16	190.48	849.86	96.12	428.87
18	13.90	68.10	1248.5	224.73	173.54	850.23	77.22	378.33
20	12.42	67.58	1259.	251.8	156.37	850.83	62.10	337.90
22	11.08	66.92	1269.	279.18	140.60	849.22	50.36	304.18
24	9.75	66.25	1280.5	307.32	124.85	848.33	40.62	276.04
26	8.54	65.46	1292.5	336.05	110.38	846.07	32.84	251.76
28	7.33	64.64	1305.	365.40	95.66	843.94	26.18	230.93
30	6.34	63.66	1318.5	395.55	83.59	839.36	21.13	212.20
32	5.35	62.65	1332.	426.24	71.26	834.50	16.71	195.78
34	4.76	61.24	1347.	457.98	64.11	824.91	14.00	180.11
36	4.17	59.83	1363.	490.68	56.85	815.47	11.59	166.19
38	3.87	58.13	1380.	524.40	53.41	802.19	10.18	152.09
40	3.57	56.43	1398.	559.20	49.91	788.89	8.92	141.25
42	3.41	54.59	1417.	595.14	48.32	773.54	8.12	129.97
44	3.26	52.74	1435.5	631.62	46.80	757.08	7.40	119.86
46	3.20	50.80	1454.	668.84	46.53	738.63	6.95	110.43
48	3.14	48.86	1473.	706.04	46.25	720.71	6.55	102.07
50	3.12	46.88	1493.5	746.75	46.60	700.15	6.24	93.76
52	3.07	44.93	1513.5	787.02	46.60	679.88	5.90	86.38
54	3.04	42.96	1534.	828.36	46.60	659.04	5.62	79.50
56	2.99	41.11	1555.	870.80	46.60	637.60	5.35	73.22
58	2.95	39.05	1576.5	914.37	46.60	615.53	5.09	67.31
60	2.91	37.09	1600.	960.00	46.60	593.40	4.85	61.81

DISCUSSION

Vice-President HOWARD: The two papers by Mr. Hooker are now open for discussion.

Secretary OLSEN: I should like to ask Mr. Hooker one question with reference to these tables and charts where you give the solubility of salt and caustic soda. Do the figures represent pure salt and pure caustic soda or the commercial grades containing various impurities?

Mr. HOOKER: The figures I have given represent *pure* NaOH and NaCl. The commercial figures for sp. gr. and saturation will differ slightly but as a rule not seriously from these due to the presence of small amounts of Na_2SO_4 and Na_2CO_3. I have some of the figures and hope some day to present curves showing saturation and sp. gr. for solutions of $NaCl+Na_2SO_4+NaOH$. However, as concentrations increase both sulphates and carbonates are largely removed together with NaCl; hence these figures without sulphates are not very far wrong commercially.

Secretary OLSEN: Therefore your curves are for pure NaOH and pure NaCl?

Mr. HOOKER: Yes.

Secretary OLSEN: And the commercial figures will differ but slightly from these?

Mr. HOOKER: Yes, very slightly.

Vice-President HOWARD: Mr. Moore, do you wish to make some reply?

Mr. MOORE: I think Mr. Hooker in his admirable paper forgot to mention one fact which I am sure he knows, and that is this: He said, when you get too high concentrations of salt it came down so fine that it would not settle down, but he forgot to mention that salt will settle down if you supply large crystals of other salt for the fine particles of salt to add thereto, building up larger crystals instead of forming new crystals of their own.

Vice-President HOWARD: Mr. Hooker, did you wish to say anything further regarding Mr. Moore's paper? Have you completed your discussion of that?

Mr. HOOKER: I think there is nothing further to discuss on Mr. Moore's paper without our studying the two problems together. I have nothing further to say.

THE EVAPORATOR EXPERIMENT STATION AT THE UNIVERSITY OF MICHIGAN

By W. L. BADGER and P. W. SHEPARD

Read at the Montreal Meeting, June 28, 1920

THE subject of cooperation between industrial concerns and universities has been discussed so frequently that this general question will not be taken up here. It is proposed, however, to describe what is believed to be a very noteworthy case of such cooperation.

During the summer of 1917, the Swenson Evaporator company of Chicago, Ill., was considering the establishment of an evaporator experiment station to study both general theoretical questions and detailed concrete problems regarding evaporator design. The possibility and desirability of cooperation in this work with some university became apparent early in the development of the idea; and the matter was taken up with the Board of Regents of the University of Michigan. After a careful and extended discussion by both parties an agreement was reached substantially as follows:

The university furnished a suitable building, light, water, steam, and power; and assumed responsibility of providing equipment or making all necessary measurements involved; this consisting of such articles as weighing devices, thermometers, gauges, manometers, recording instruments, volumetric measuring devices, etc. The Swenson Evaporator Company bore the entire expense of designing, building and erecting the machinery; and as soon as erected, its title passed to the University of Michigan. The whole station then, is the property of the university and is available for instruction, demonstration and research. In return for this investment the university granted to the Swenson Evaporator Company the right to carry out certain detailed investigations of its own; the right to maintain in this laboratory its own employees and the right to retain as its own property the results of certain specific classes of detailed investigation. It was expressly provided, however, that in case any facts of general scientific importance were developed, they were to

become public property even though they were developed by the company's employees and at the company's expense.

The design of the apparatus was immediately started; but its manufacture and delivery were greatly delayed due to conditions arising out of the war. The actual equipping of the laboratory did not begin till March, 1918. The principal equipment was added as rapidly as possible, but the final layout was not ready till August, 1919. Due to lack of graduate Chemical Engineering students during the war, the work so far has been largely carried out by the company's employees and at the company's expense. The two papers accompanying this description fall in this class. Acknowledgment is made to Mr. E. M. Baker, Instructor in Chemical Engineering in the University of Michigan, who has taken an active part in the development of the laboratory and the prosecution of the research.

The principle adopted in planning the equipment was to make all units large enough to minimize personal errors and errors due to small-scale work. The station was to furnish data for actual engineering design; not only for evaporators but for entire plants and complete processes. Consequently all units installed were of commercial size; and results obtained in them are transferable quantitatively to full-scale commercial operation. Much thought was given to all possible problems, both general and specific, which might arise. Provisions were accordingly made for changing the set-up and connections, taking temperature and pressure measurements, and in general anticipating the requirements of the most varied and intricate work which could be expected. Attention was given to making it possible to secure ample data for every step of an experiment. Every problem, both general and specific, which the station takes up, is treated quantitatively. This is not only for the sake of collecting a general fund of information regarding the behavior of evaporators, but also that all possible problems, which might arise in development of the process experimented on, might be forestalled.

Since the primary purpose was to study evaporator design, one representative of each of the three common types of evaporators was provided. Accordingly the station has a vertical tube, a horizontal tube, and a film type evaporator following the standard designs of the Swenson Evaporator Company for each type. To handle problems where crystals are deposited there is a salt filter which may be used on either the horizontal or vertical tube evaporator.

To make possible the solution of the widest variety of problems, the heating surfaces of each evaporator were made easily removable and a

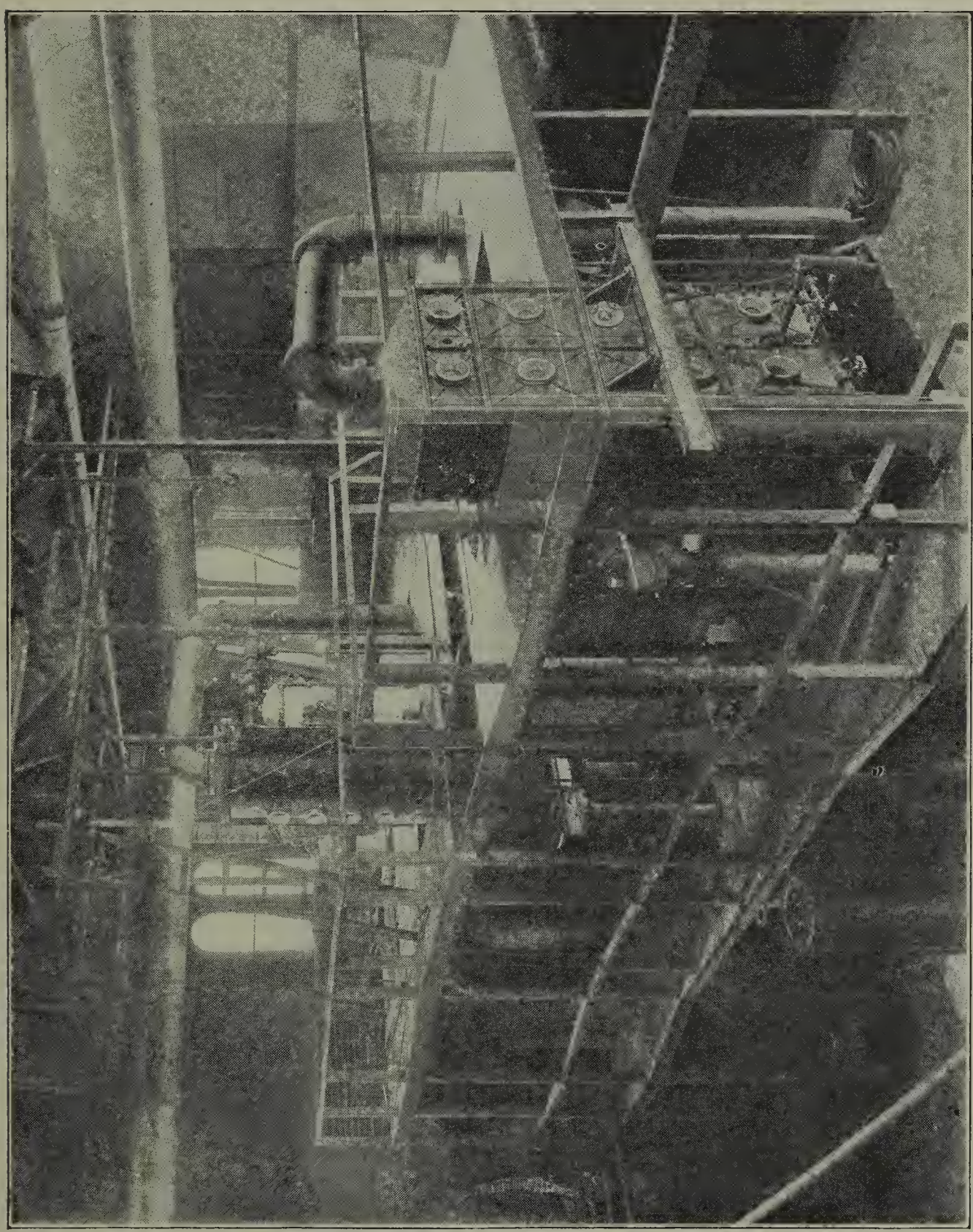


Fig. 1.—General View of Evaporator Experiment Station, Showing Working Platforms, Vertical and Horizontal Tube Evaporators.

wide variety of methods of disposing or arranging the heating surfaces was provided. Parts forming vapor belts were made interchangeable so that the main dimensions of the machines could be

altered at will. Several types of bottoms were provided and made easily removable and interchangeable.

The station also possesses a number of storage tanks, so that

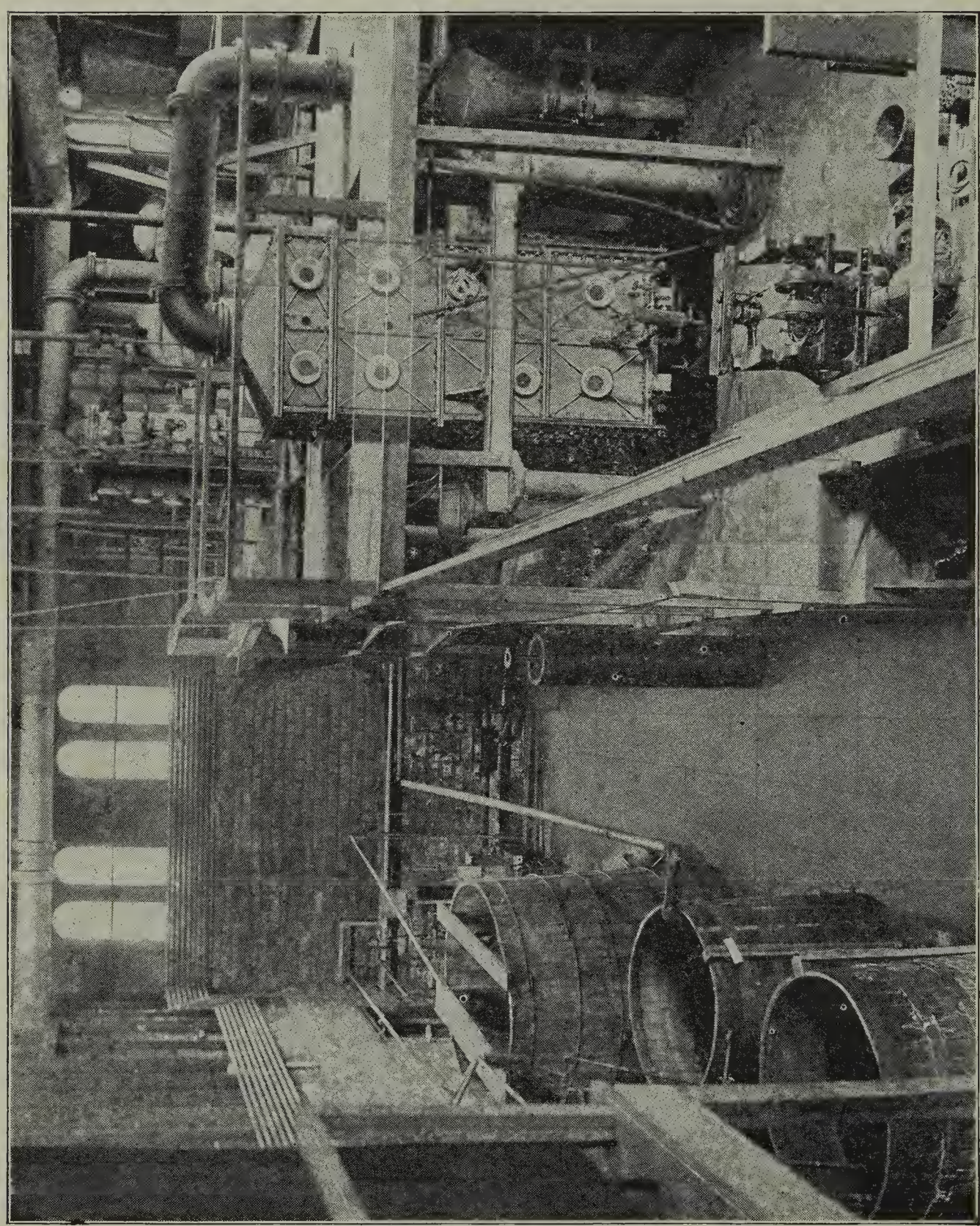


Fig. 2.—General View of Evaporator Experiment Station. Horizontal evaporator and centrifugal in foreground. 7′0″ steam basket for vertical evaporator on floor near center.

several materials may be on hand at one time. Capacity is provided for storing a tank car of liquid. Pumps and pipe lines make all possible combinations available. One tank is provided with an agitator for making up solutions.

Operations of interest to the chemical engineer other than evaporation have not received as much attention as evaporation but are being added rapidly. A filter, a centrifugal, a crystallizer and a steam-jacketed kettle are now installed.

The station is housed in a building which was formerly the University power house. The old boiler room contains the laboratory proper. This is 65×35 feet in plan; the floor is 15 feet below ground level, and the roof extends in part to a height of 35 feet, giving ample head room. This room still contains the University's distribution system for steam, electricity and water, though the mains are now supplied from a new power house. A bunker 60×20 feet is available for storage. The room is very well adapted for the purposes of the work that will be done. In the front part of the building is an office and a drafting room for the use of the station staff. A good idea of this building is given in Fig. 1 and 2.

Vertical Tube Evaporator

The vertical tube evaporator, Fig. 3, is of the Swenson patented basket type. This choice was made not only because the Swenson Evaporator Company was naturally most interested in this type of evaporator (as representative of vertical tube machines), but also because it made alterations of the heating surface much simpler. The body of the evaporator is of cast iron, 30 inches in diameter, and is built in 4-foot sections. The bottom section carries connections for feed and wash water. Condensed steam from the basket is taken out through a stuffing box in this section. Intermediate sections have no pipe connections in ordinary operations. A pad is provided along one side of all sections. This carries a number of openings tapped for 2-inch and $\frac{3}{4}$-inch pipe. All ordinary connections are made through these openings; and such special piping as may become necessary is thus anticipated. The top section carries the steam connections. A $1\frac{1}{2}$-inch line brings steam at about 100 pounds and a 3-inch line brings steam at about 3 pounds. These unite in a tee into a 3-inch line which passes through the top section and down the center of the evaporator to the steam basket. Some runs have been made with the top and bottom sections only, making the evaporator 8 feet high. Most of the work has been done with one intermediate section making the evaporator 12 feet high. (See Fig. 4.) Another intermediate section is provided so that the evaporator can

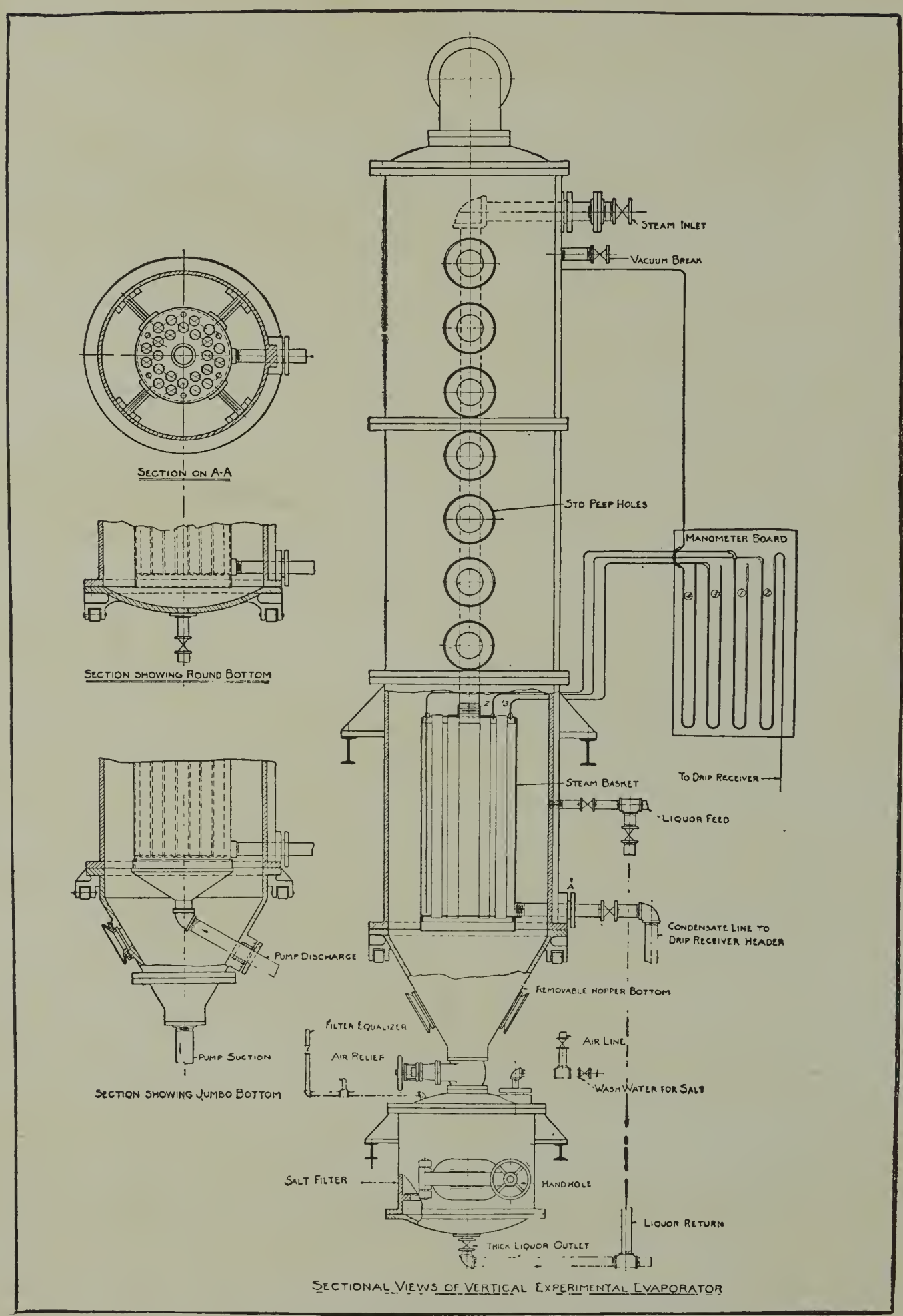


Fig. 3.—Diagrammatic Sketch of Vertical Tube Evaporator

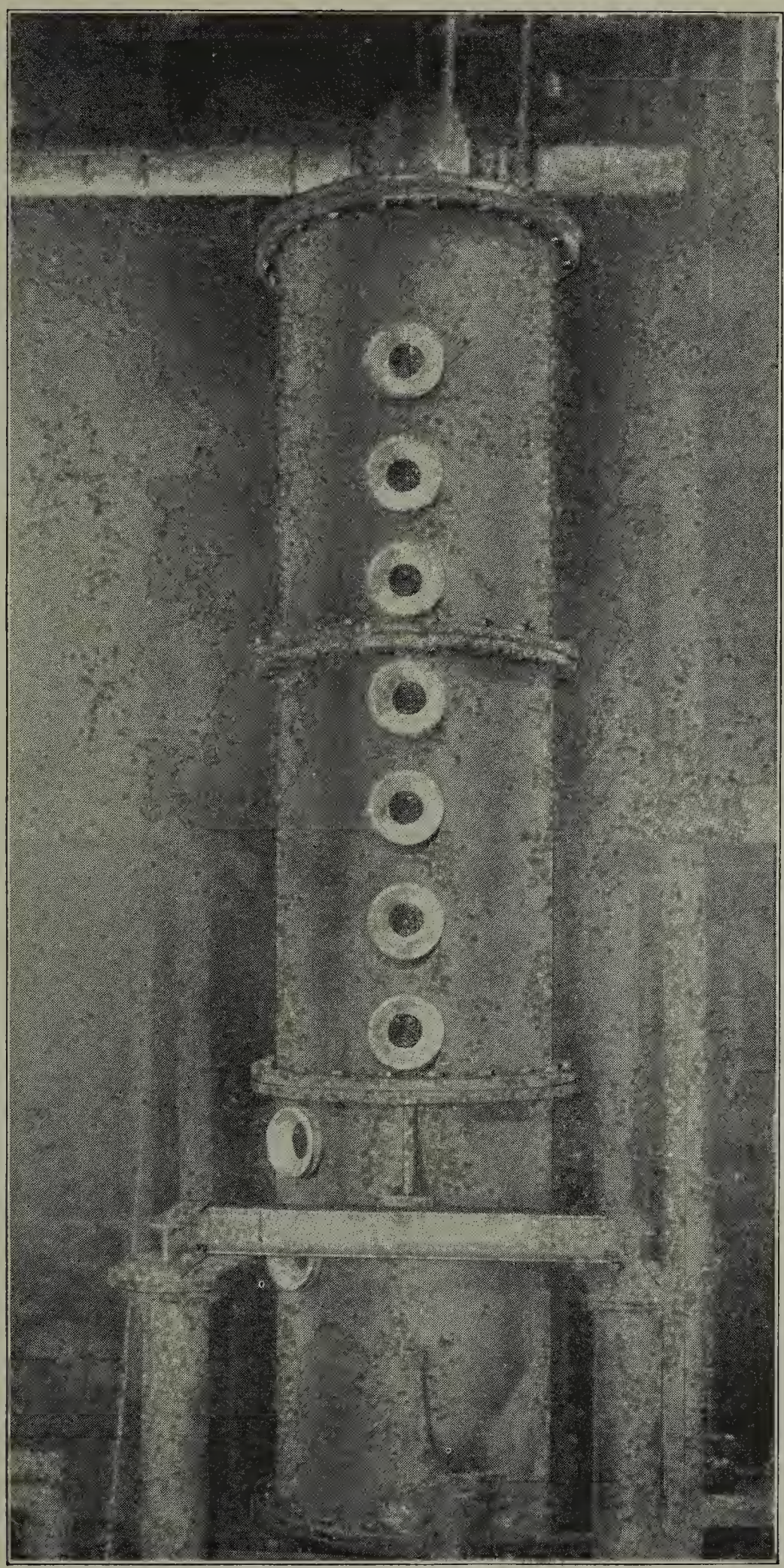


FIG. 4.—Front View of Vertical Tube Evaporator.

be carried to a height of 16 feet if desired. The vapors are removed from the evaporator by a 10-inch cast-iron pipe to a wet parallel current condenser which, instead of being mounted near the top of the evaporator, as is customary, is located on the operating floor so as to be available for test.

The steam baskets provided for this evaporator are all of 18-inch O. D. and carry twenty-four 2-inch charcoal-iron tubes. They have a 3-inch central steam inlet and six $\frac{1}{2}$-inch connections around the outside edge of the top head for manometer connections, etc. Condensed steam is removed by a 2-inch pipe flush with the bottom head. Four baskets are at present provided with tubes respectively 30 inches, 48 inches, 60 inches, and 84 inches long. Baskets of this diameter give an annular down-take space of 6 inches. This makes a very much larger ratio of down-take area to tube cross-section than is usual, but this was done purposely. The question of the proper value for this ratio is a rather important one on which no direct evidence is available. Sheet-iron filler cylinders are provided to reduce the diameter of the machine at the level of the steam basket so that the down-take ratio can be varied and the effect of changes in the ratio may be studied. This problem has not yet been taken up. The purpose of providing baskets of different tube lengths was mainly to study the question of ratio of tube length to tube diameter. Considerable work has been done on this, but the results will not be ready to report for some time.

The evaporator is provided with three bottoms; a flat bottom, a 60° cone bottom, and a special cone bottom with provision for forced recirculation by an arrangement patented by the Swenson Evaporator Company (called the " Jumbo " bottom). A salt filter, 24 inches in diameter and 18 inches high is mounted on a truck at such a height that it may be connected by a 3-inch gate valve to the standard hopper bottom. Set screws in the brackets of this filter make its exact adjustment a simple matter. The filter is provided with monel metal screen held between two heavy perforated plates. (See Figs. 5 and 6.)

The evaporator is set so that the bottom flange of the lower section is about 8 feet from the ground floor. An overhead trolley is provided for handling heavy parts. The various bottoms have brackets bearing rollers. Removable tracks may be quickly bolted to the columns which support the evaporator. When it is desired to change the bottoms on the evaporator, the tracks are put in place, the bottom

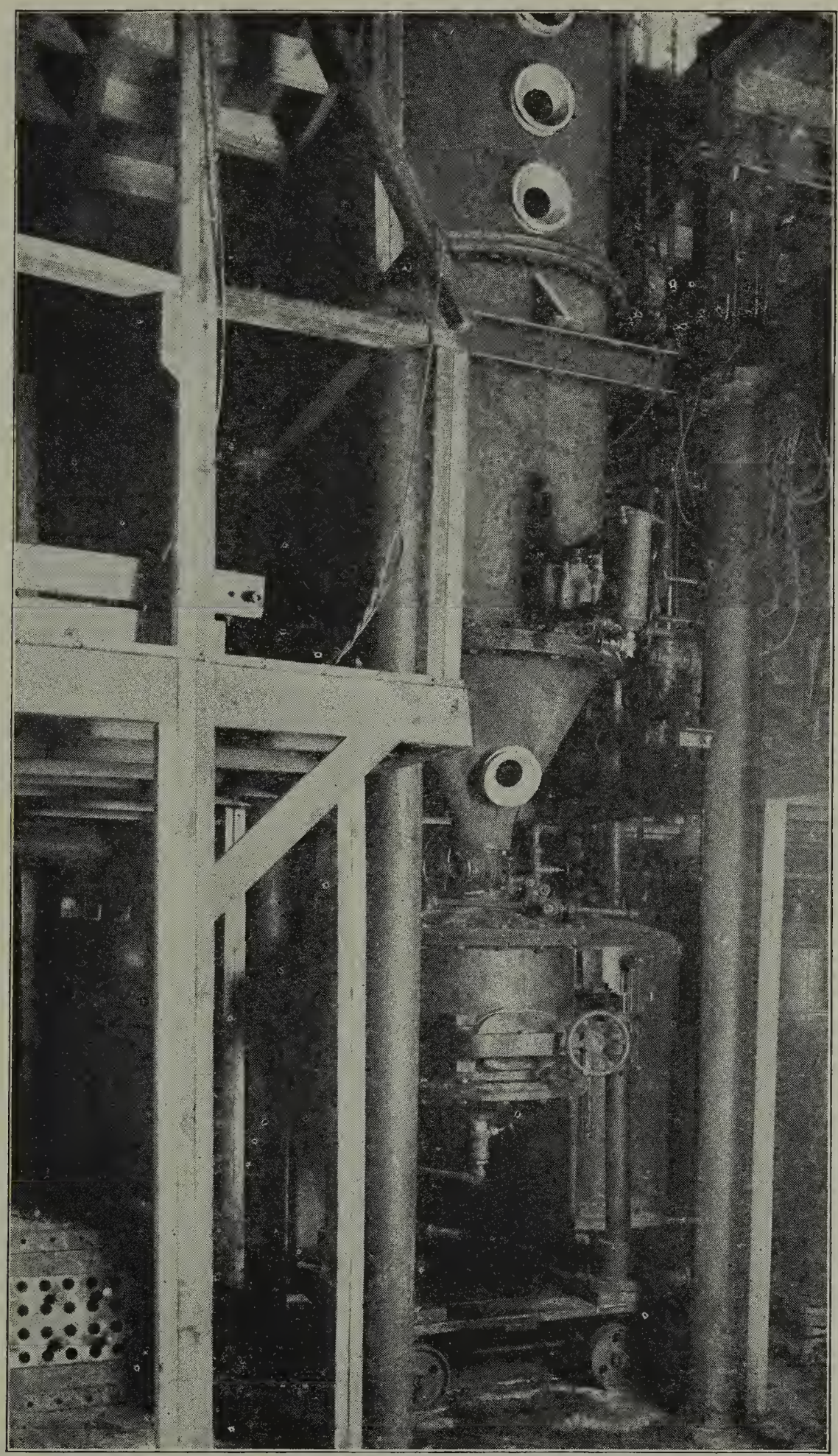


FIG. 5.—Vertical Tube Evaporator with Cone Bottom and Salt Filter.

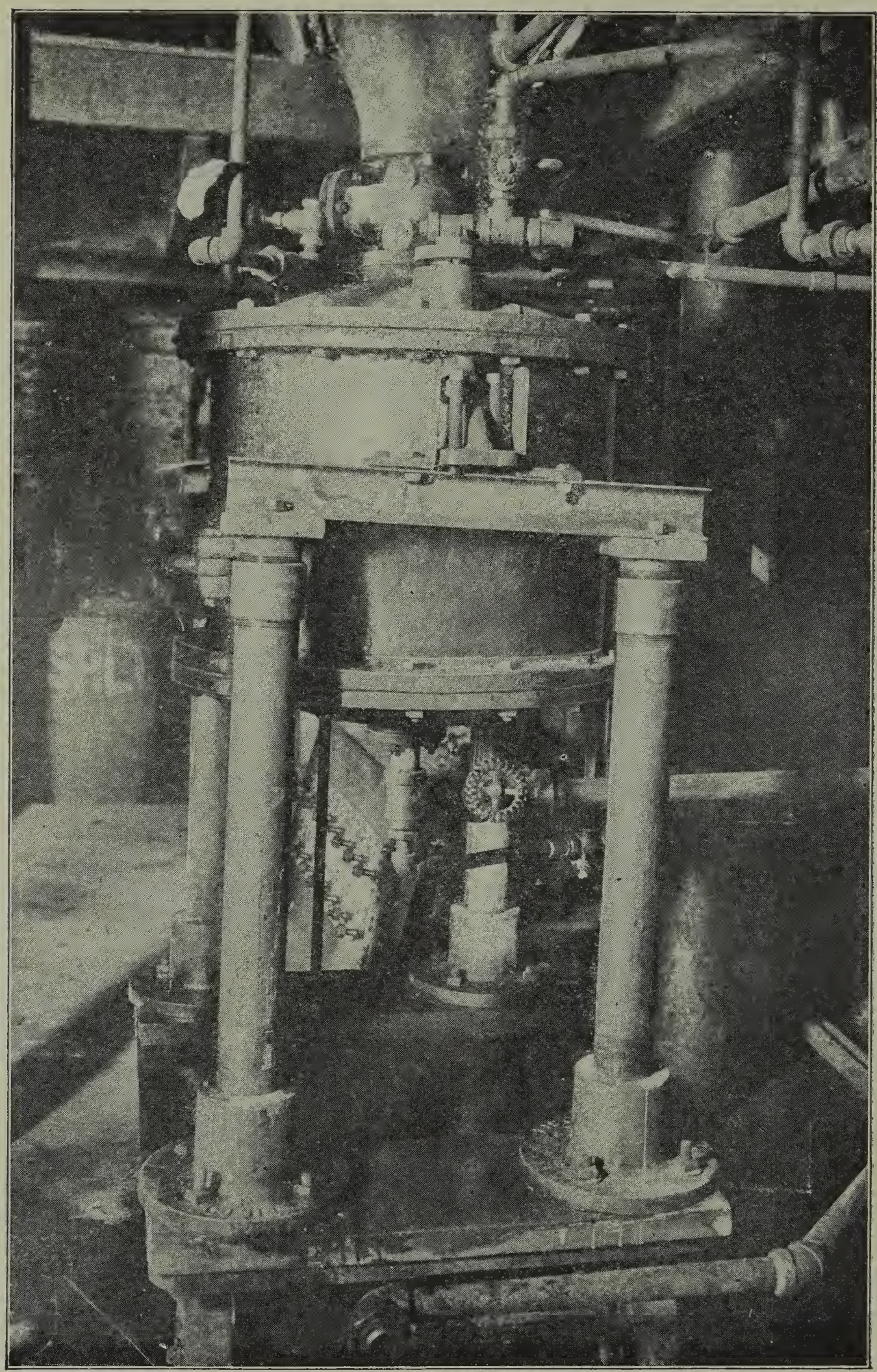


Fig. 6.—Side View of Salt Filter.

which is in service is unbolted and lowered to the tracks (about 2 inches), rolled from under the machine, and removed by the chain-falls. The new bottom is hoisted on the tracks, run under the machine and lifted into place by drawing up the bolts.

Horizontal Tube Evaporator

The horizontal tube evaporator (see Figs. 7 and 8), is approximately 30 inches wide by 4 feet long inside, made of ribbed rectangular cast-iron plates. The ends of the evaporator in ordinary commercial design are the tube sheets. In this evaporator in order to make changes simple, the sides and bottom are assembled on a cast-iron frame called the front plate; and to this front plate is bolted the tube sheet. This makes it possible to change tube sheets; thereby permitting the study of such problems as varying the diameter of the tubes, varying their spacing, putting in circulation belts, etc. The tube sheets generally used take $\frac{7}{8}$ inch O.D. tubes, on $1\frac{5}{8}$-inch centers. This makes room for 16 tubes in each horizontal row and 28 in each vertical row. It is not intended that all these be used at once. Generally from 40 to 75 tubes are used. They have an effective length of 3 feet 10 inches and a heating surface of 0.75 square foot per tube. The steam chests are cast box shape and have condensate drains from the bottom of each. Several vapor belts, each 27 inches wide, are provided, and the minimum height of machine is about 5 feet. This evaporator is also provided with a 10-inch vapor pipe, and its condenser is the same as the one on the vertical. Like the vertical evaporator, it is mounted on brackets so that the bottom is entirely unobstructed. It is provided with a flat bottom and also with a hopper bottom. It is set at such a height that when it is equipped with the hopper bottom the salt filter which serves the vertical evaporator will fit it also. The salt filter is mounted on a truck which makes it easy to transfer from one evaporator to the other. The hopper bottom is provided with a stuffing box so that the effect of forced circulation may be tried here also.

Semi-Film Evaporator

This evaporator (see Figs. 9 and 10) is the third representative in the station and offers several interesting features. It is patented by the Swenson Evaporator Company and is known as their " Type

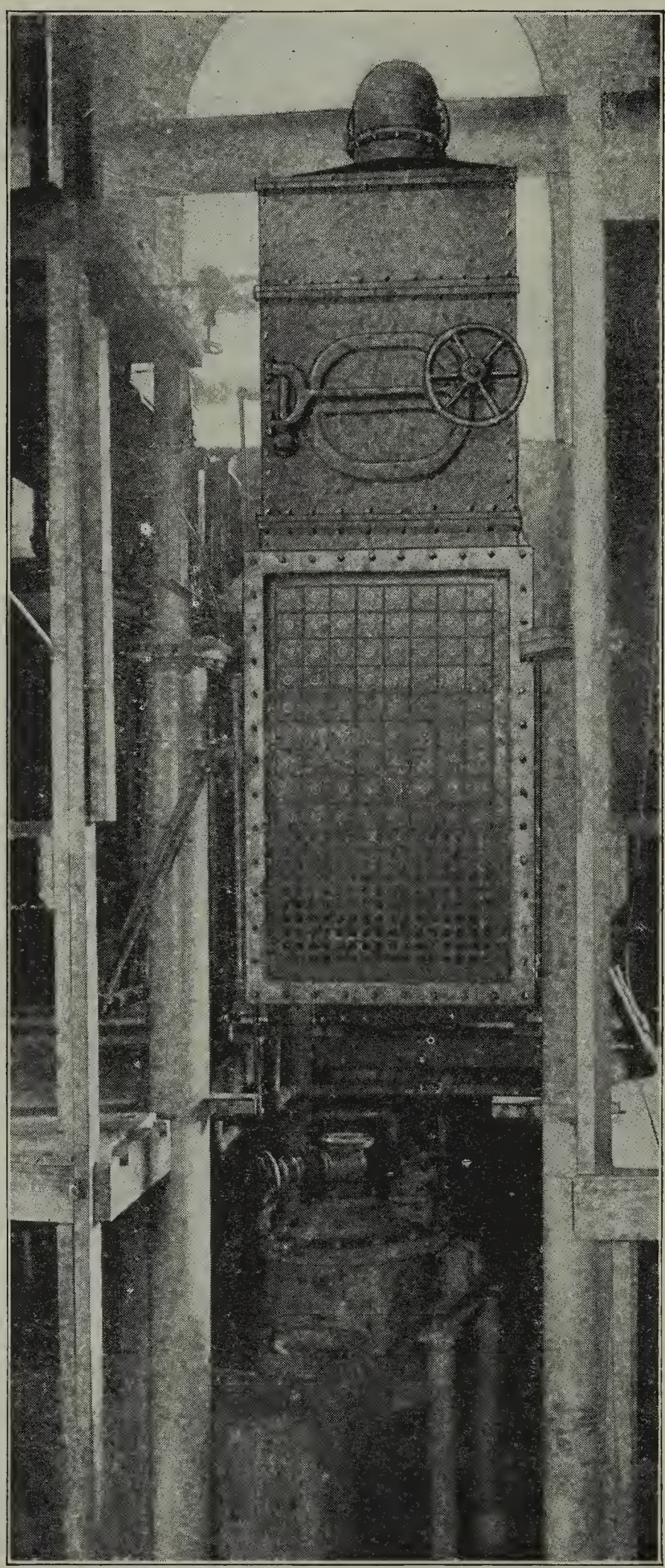


FIG. 7.—Front View of Horizontal Tube Evaporator with Steam Chest Cover removed showing Tube Sheet.

K" evaporator. It is primarily a horizontal tube evaporator similar to that just described except that it is only about 15 inches wide. It carries, however, 2-inch tubes. Corresponding to the steam chests of the horizontal tube evaporator are two steam belts, one on

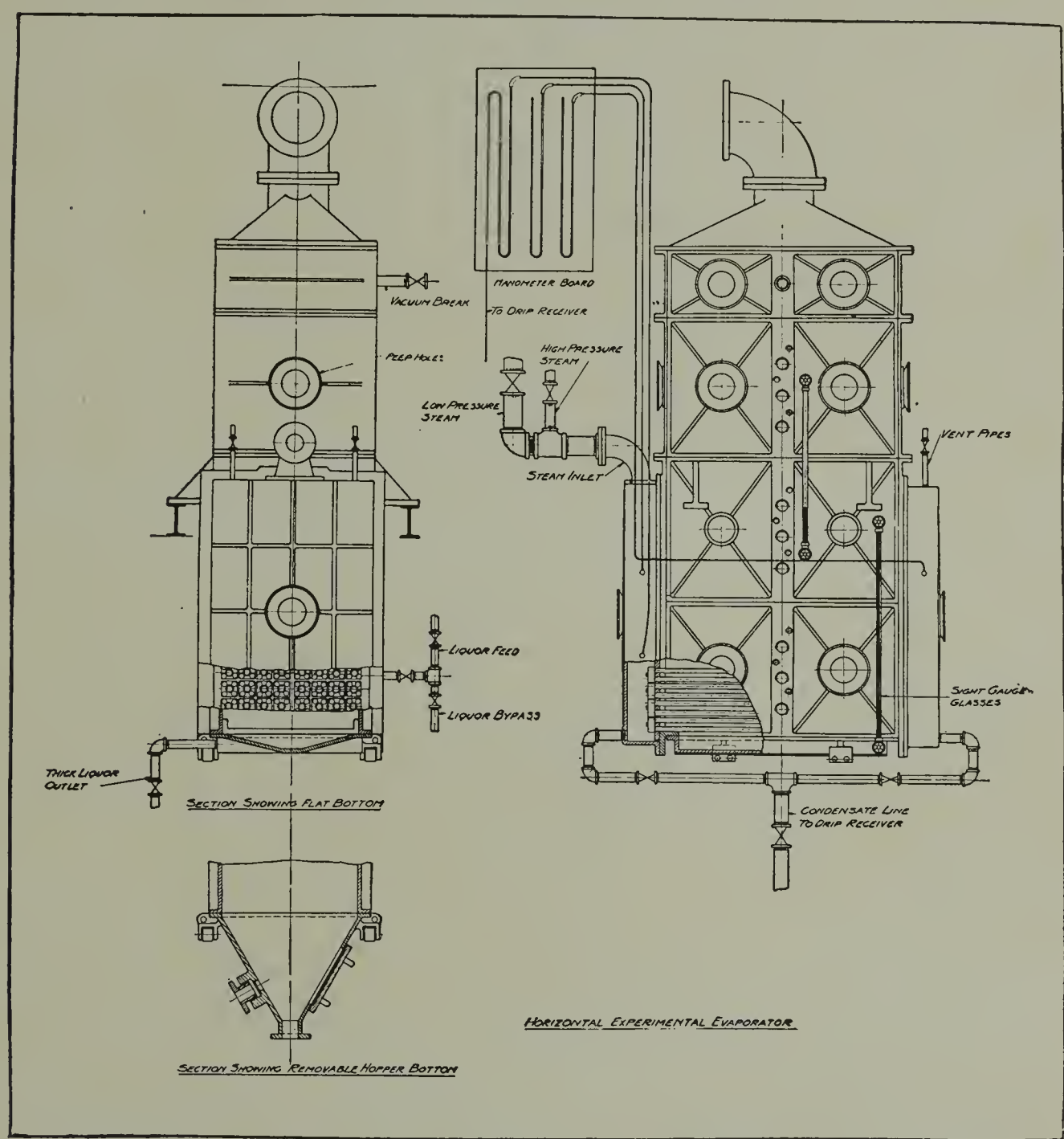


Fig. 8.—Diagrammatic Sketch of Horizontal Tube Evaporator.

either end; and these steam belts instead of being closed by a cover plate as in the ordinary horizontal evaporator, are closed by secondary tube sheets. These secondary tube sheets carry $1\frac{1}{4}$-inch tubes concentric with the 2-inch tubes in the primary tube sheet. These $1\frac{1}{4}$-inch tubes are connected in series on the outside of the evaporator by means of special return bends.

Steam is passed into one of the steam belts and thus enters the annular spaces between the 2-inch and the $1\frac{1}{4}$-inch tubes. The liquid to be evaporated is pumped into one of the return bends and circulated back and forth through all $1\frac{1}{4}$-inch tubes in series. From the last return bend it is discharged into the body of the evaporator where it is boiled by the 2-inch tubes as in an ordinary horizontal evaporator. It is possible in the operation of this machine to

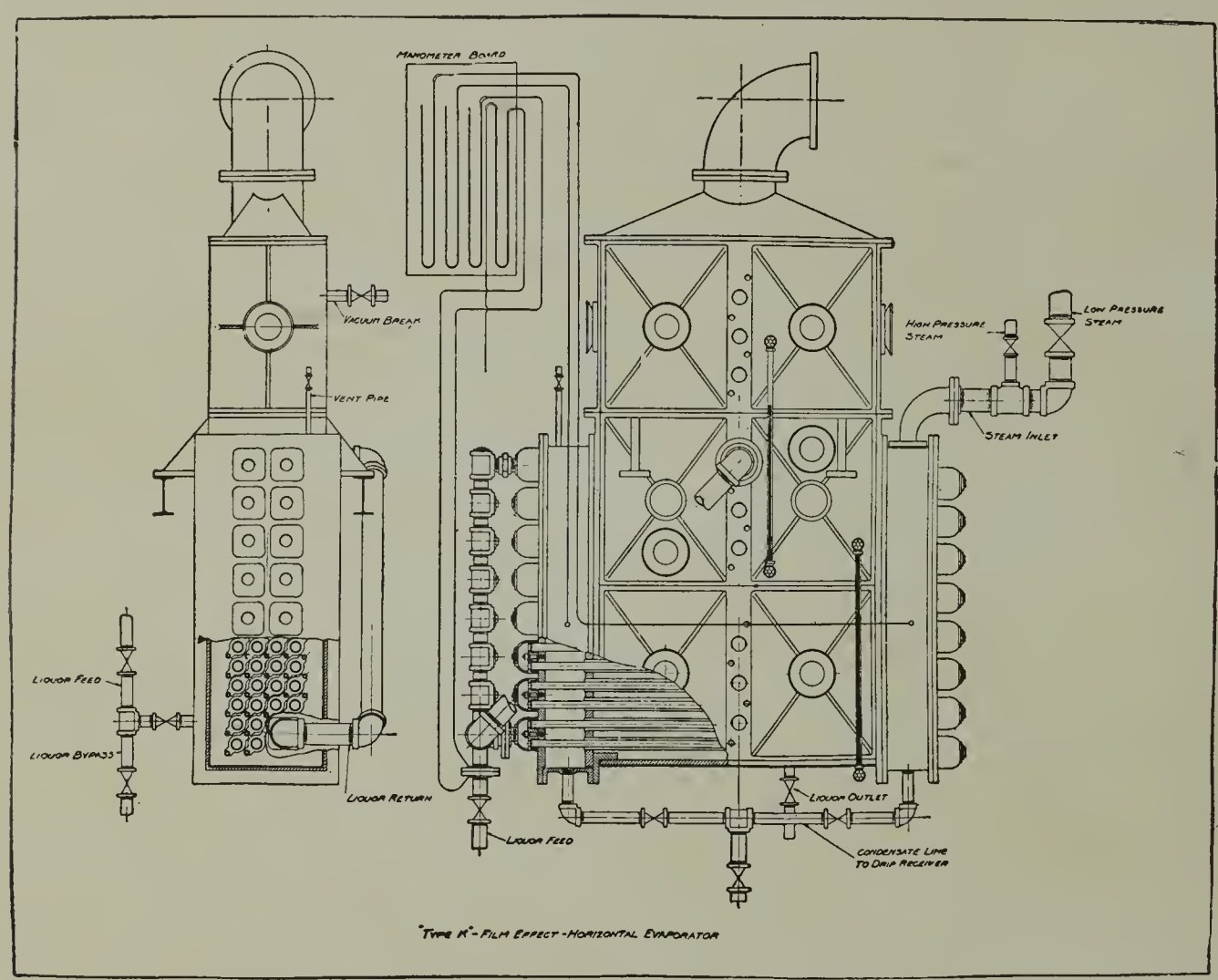


Fig. 9.—Diagrammatic Sketch of Type K Semi-film Evaporator.

separate the inside tubes from the outside tubes and thus a very wide ranage of interesting problems is opened up.

Condensate Receivers

The whole subject of the basis for reporting the results of the station has been given careful consideration, and it has been decided to base all work on the actual heat transmitted rather than on amount of liquid evaporated. The latter plan obscures the results by introducing such factors as temperature of feed, loss by entrainment,

radiation, etc. All these may be determined when desired; but the fundamental work is based on heat transmitted. Therefore the

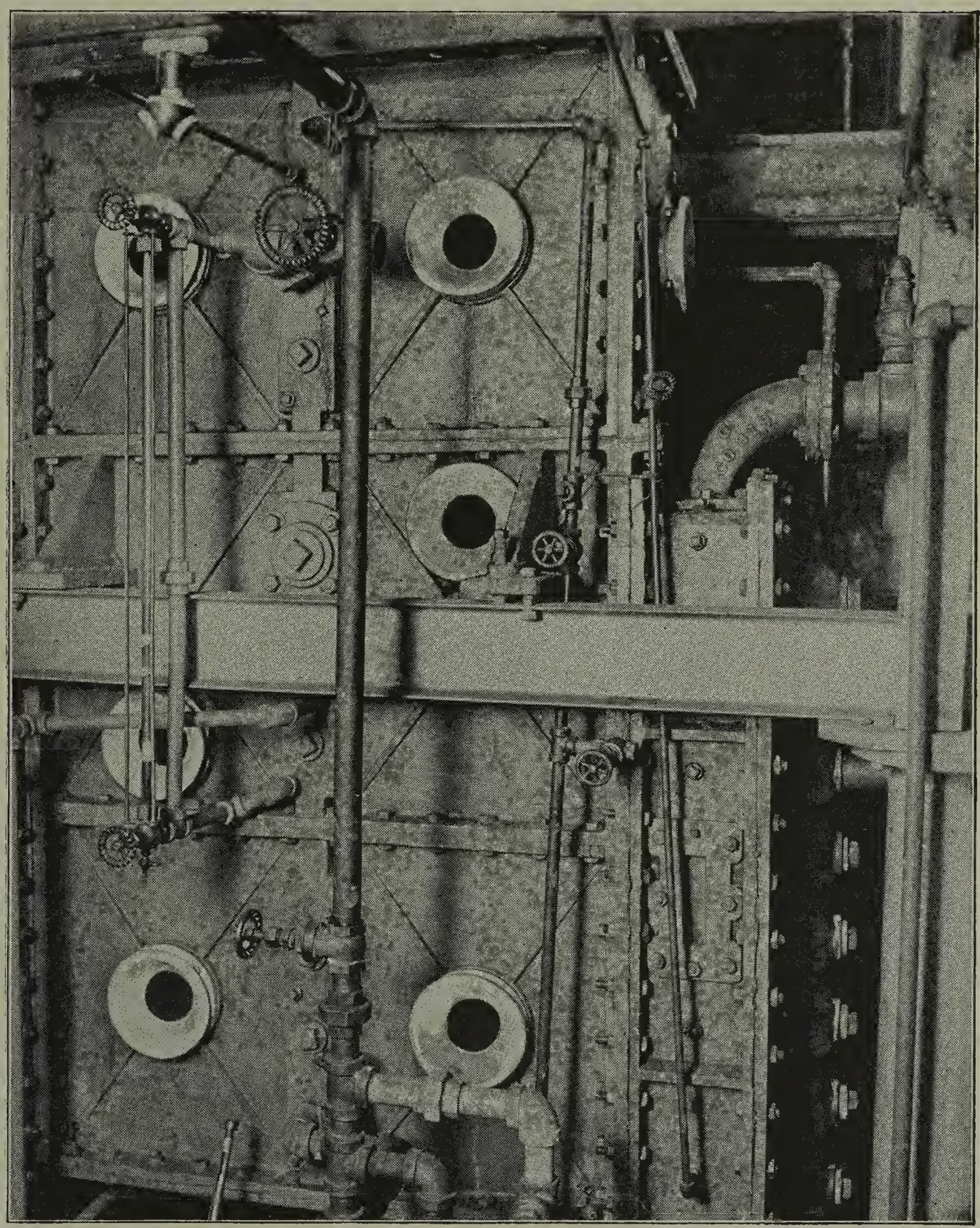


FIG. 10.—Type K Evaporator.

primary measurement is the weight of steam condensed in a given time.

This is determined by collecting the condensate in receivers

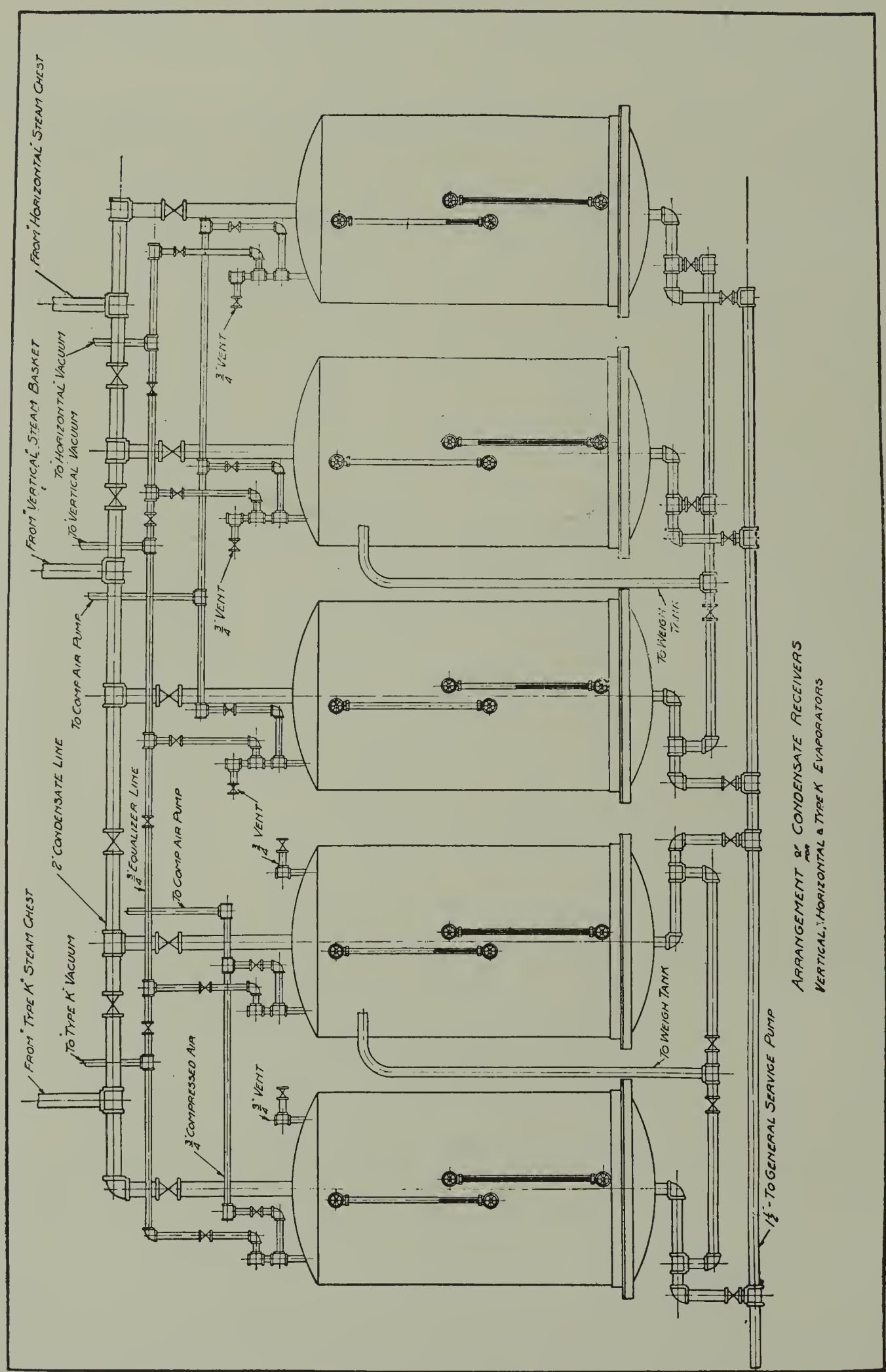


FIG. 11.—Arrangement of Condensed Water Receivers.

(see Figs. 11 and 12); in which it may be measured or from which it may be removed and weighed. There are five of these sheet-iron tanks 30 inches in diameter, 48 inches high, with heavy cast-iron bottoms and sheet-iron heads. They are all connected into a 2-inch header. Into this header come connections bringing the condensate from the various evaporators. The headers and their valves are so arranged that all the evaporators may run at the same time or

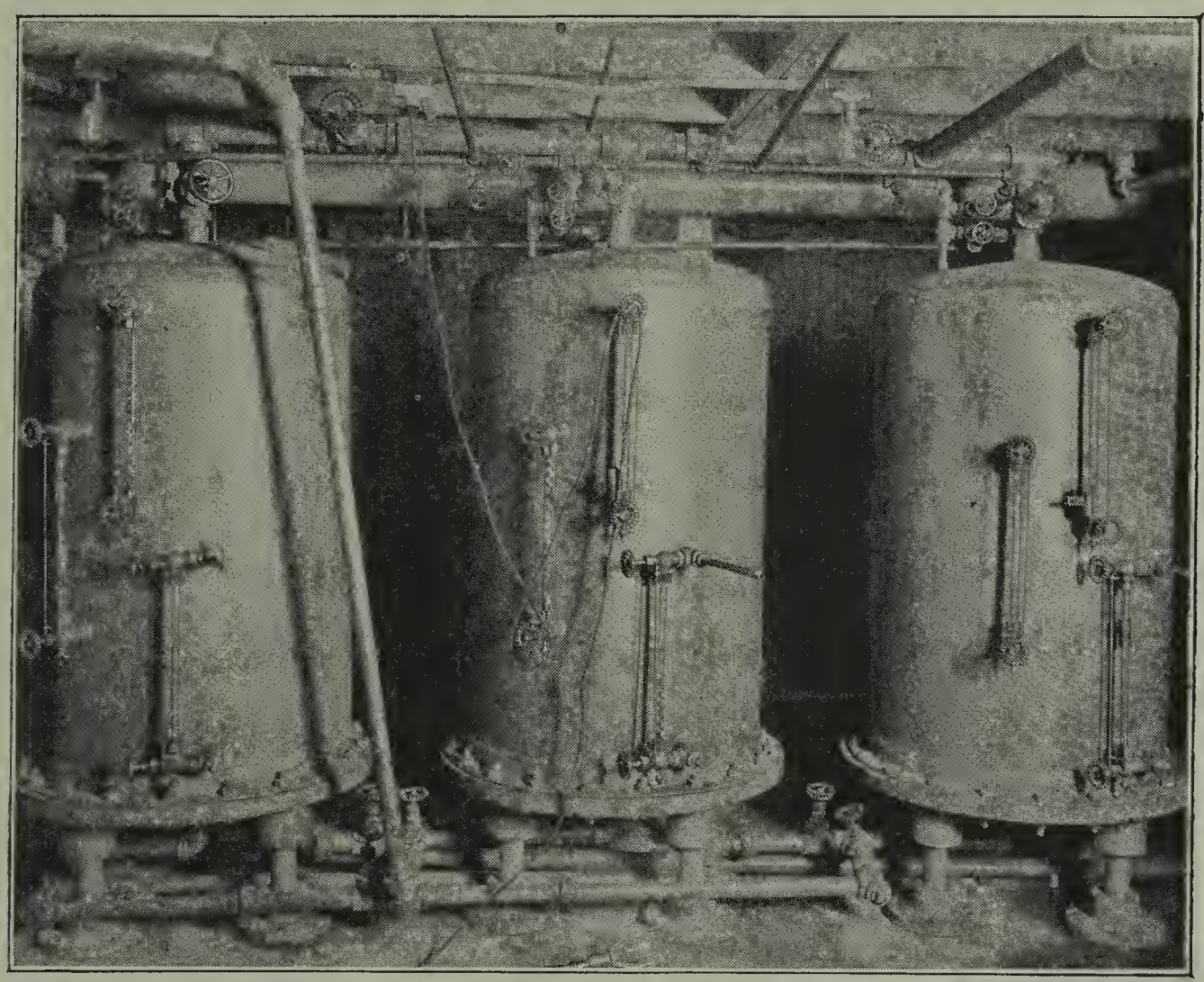


FIG. 12.—Condensed Water Receivers.

more than one receiver may be provided for runs where large amounts of steam are condensed.

In order to vent these receivers and also to remove non-condensed gases, each receiver has a $\frac{1}{2}$-inch vent connected to a $\frac{1}{2}$-inch header. This header in turn has three $\frac{1}{2}$-inch vent lines, each with throttling and blow-off valves, running one to each evaporator. Suitable valves make it possible to vent any receiver to any evaporator. These vents, during a run, are throttled down to the point where they just serve to keep the steam space clear of non-condensed gases.

A header delivers compressed air to each receiver. The bottom

outlets have two headers. One delivers to a gooseneck which discharges into a weigh tank, the other leads to the general service pump. Each receiver has carefully calibrated gauge glasses, and a ther-

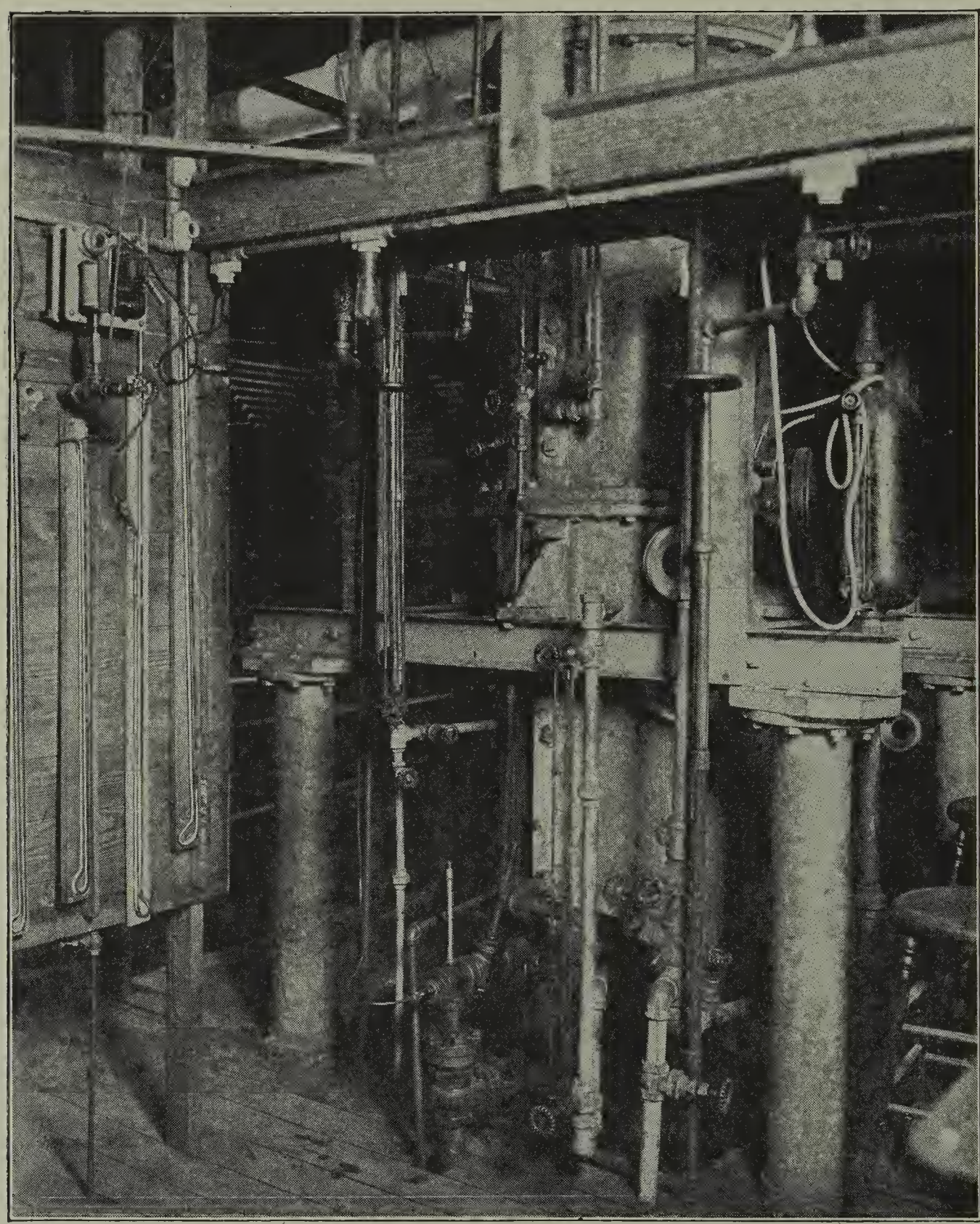


FIG. 13.—Working Platforms and Controls on Vertical Tube Evaporator.

mometer for calculating density corrections to the calibrations. During a run the condensate level is noted at the beginning and at the end. The quantity may be calculated from the calibration; or

compressed air turned in and the condensate blown over into the weigh tank. This latter method, of course, can be used only when the condensate is below 100°.

In spite of the large size of the equipment and its complexity, a highly centralized control system has been developed. From the

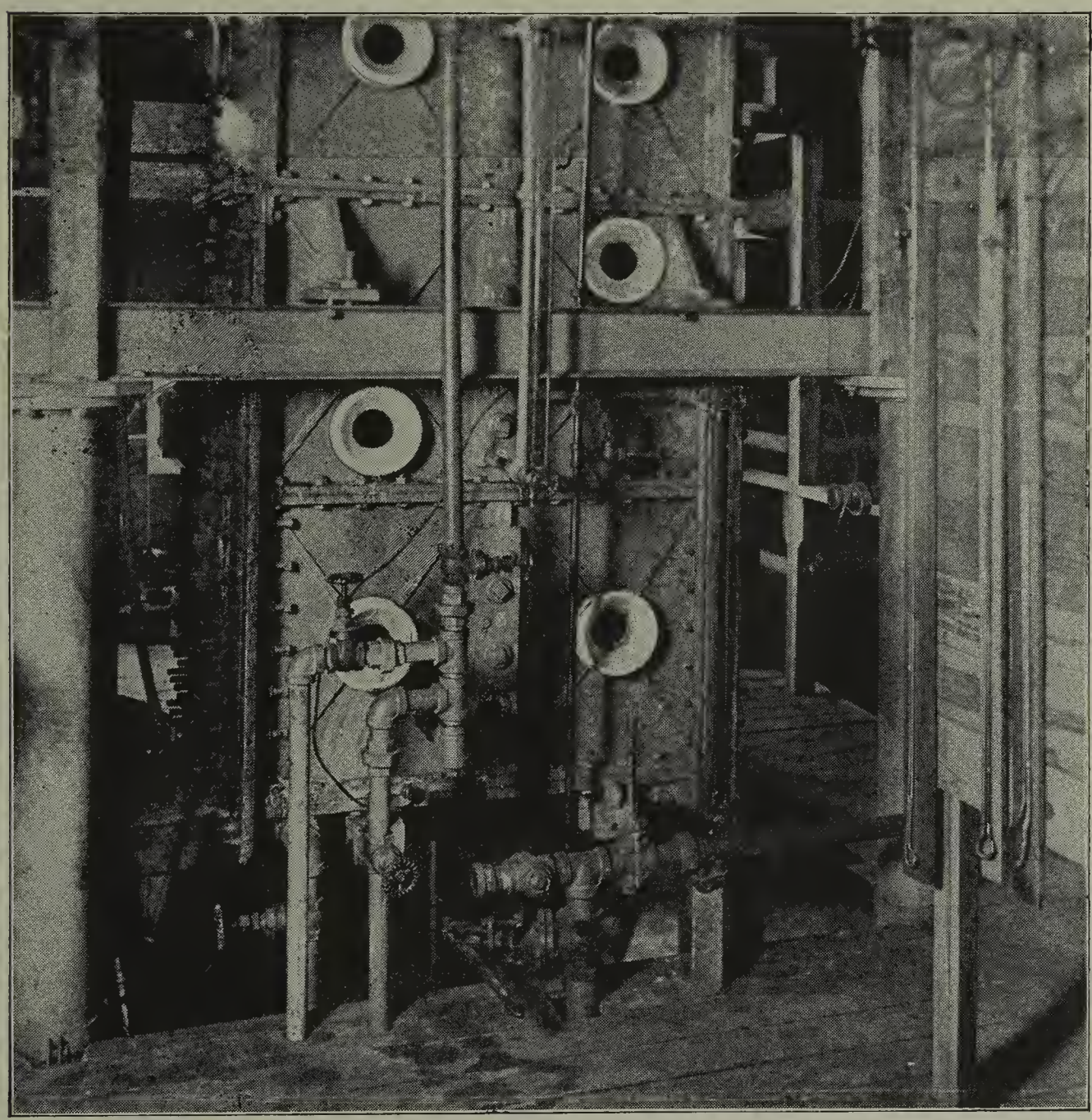


Fig. 14.—Working Platforms and Controls for Horizontal Tube Evaporator.

working platform, 7 feet 6 inches above the floor, one man can operate each evaporator and take all necessary readings. Steam, feed, condensate, vent and all other valves may be reached from one position, immediately in from of the manometer board. The condenser and vacuum pump are also controlled from this floor.

Fig. 13 shows the controls on the vertical evaporator, and Fig. 14 on the horizontal.

All pressure measurements are made with mercury manometers connected by seamless copper tubing to the point where pressure is to be determined. All manometers for one evaporator are collected on a manometer board near the controls. Temperatures are measured by calibrated thermometers, protected by iron pipe guards. All measurements are taken in the metric system; partly because accurate laboratory apparatus is usually metric, partly because of simplicity of calculation, and partly because practically all of the literature on evaporator design is in German and hence comparisons with previous work are easier if results are in metric units.

Early in the work it was found that maintaining an accurately controlled vacuum was rather difficult. A vacuum regulator was devised which has been very satisfactory (see Fig. 13). A $\frac{1}{2}$-inch pipe is led from the top of the vapor space to the instrument board and carries a Crane needle valve opening to the air. It also carries a special needle valve with no stuffing box around the stem. This stem is prolonged and is connected to a bar of soft iron which forms the core of a solenoid. An iron wire is immersed in the mercury in the open arm of the vacuum manometer. A brass rod ending in a platinum-tipped wire passes through a stuffing box into the high side of the vacuum manometer. This rod is threaded and its position may be very accurately adjusted by a milled nut in a small bracket on the instrument board. The vacuum pump is run a little faster than necessary to maintain the desired vacuum. As the mercury in the vacuum manometer rises and reaches the desired point, it makes contact with the platinum tipped brass rod and thereby closes a circuit through an ordinary telegraph relay. This relay closes a 220-volt circuit through the solenoid, opens the needle valve and bleeds air into the vapor space of the evaporator until the vacuum falls to the desired point. The second needle valve above mentioned is set by hand to give an approximation and the regulator is thus left to take care of only minor fluctuations. The device has worked very satisfactorily and will usually hold the vacuum to within two millimeters for an indefinite length of time. Occasionally the strokes of the vacuum pump become synchronized with the natural period of vibration of the mercury, which produces regular surges in the manometer with a slight decrease in the accuracy of regulation.

An upper platform, 15 feet above the floor, is provided for giving

access to the upper parts of the evaporators. Weigh tanks and feed tanks, one of each for each evaporator, are located here. When desired, the feed may be weighed, but this is not often necessary. This obviates maintaining an operator on the upper floor during a test. The station is surrounded by a balcony at this level connecting with these upper platforms and with the office.

General Equipment

The station is served by a $1\frac{1}{4}$-inch Class " C " Worthington Volute Pump. By means of a manifold on the suction and another manifold on the discharge this pump performs practically all the work of the station. One ring discharge main extends around the station connecting with all the storage tanks and evaporator feed tanks. The common suction line is not a complete ring but includes all the storage tanks on one side and all the evaporators on the other side. There are a number of separate connections besides these two principle mains. A Marsh $3 \times 5 \times 8$ Magma Pump is connected into the suction line and into the ring main; and valves are so placed that it may be used either as a substitute for the general service pump, or operated in parallel with, but independent of, the general service pump.

The three condensers unite in a cross and the fourth outlet of this cross is connected to an American-Marsh $8 \times 10 \times 12$ vacuum pump. Valves are placed in the lines to the condensers so that evaporators not in use can be completely cut off. This pump and the magma pump mentioned before are a gift to the laboratory from the American Steam Pump Company of Battle Creek. A small direct steam-driven air compressor furnishes air at 25 pounds; city water at 60 pounds, and 200-volt direct current are furnished from the university mains. The floor of the station is below the sewer. Waste water is consequently discharged into a sump from which it is lifted by a Worthington Duplex $5\frac{1}{4} \times 4\frac{3}{4} \times 5$ tank pump, the gift of the Henry R. Worthington Co. The station also has a 10-inch experimental centrifugal (see Fig. 1), loaned by the American Tool and Machine Co., and a No. 2 Sweetland Filter, loaned by the United Filters Co. A crystallizer, a steam jacketed still, and additional transfer pumps will be added in the immediate future. A Tagliabue Liquor Level regulator, loaned by the Tagliabue Mfg. Co., has very greatly simplified the experimental work on the vertical tube evaporator.

Program

The work of the station falls into two very distinct classes. The first, by far the more important, is the class of purely theoretical investigations into the principles of evaporator design. Two papers, the first results of this program, are being presented herewith. These two deal with the vertical tube evaporator because the staff of the station has been insufficient to keep work going continuously on all three evaporators. A great deal has already been done on the horizontal tube evaporator and the "type K" evaporator, but no results are ready for publication from these machines. The program of problems already outlined involves over sixty separate questions, illustrations of which are the problems already mentioned in connection with the vertical tube and horizontal tube evaporators. It is hoped that it will be possible to publish a continuous series of papers along these lines; and the volume of work so available depends primarily on the growth of the graduate work in the chemical engineering department of the University of Michigan.

The second class of work in which the station is engaged is in the solving of concrete problems regarding the development of a particular process or the evaporation of particular solutions. As a sample of the types of problems already handled may be mentioned the following: The production of high-grade table salt from dilute brine carrying much larger amounts of calcium and magnesium chlorides than is considered practicable in ordinary salt manufacture; the preparation of a high-grade potash salt from an impure western brine carrying sulphates, chlorides and carbonates of both potassium and sodium; the evaporation of dextrin syrup to high concentration; the design of a lead evaporator for the manufacture of aluminum sulphate, etc.

The station was originally planned to study evaporators only and consequently no accessory apparatus such as filters, centrifuges, etc., was planned. The size and scope of the concrete problems which have come up, have made necessary a revision of this plan and it is intended now to extend the equipment of the station until there will be in existence a complete chemical plant with all its units on the scale of the evaporators. This will mean that complete processes can be worked through in ton lots. It takes at least 1000 gallons of a solution to make a satisfactory test so far as the evaporators are concerned. This station is not interested in the working

out of new processes on the usual chemical laboratory scale, as there are other organizations much better fitted to handle that class of research work, but we are interested in the working out on a commercial scale, of processes already established in a chemical laboratory.

Interesting though these specific problems are, it is not intended that they shall ever displace the principal purpose for which the station was founded; which is the study of the underlying principles of evaporator design and through them the extension of our knowledge of the whole phenomenon of heat transmission from steam to liquids.

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Edward Bartow

STUDIES IN EVAPORATOR DESIGN. I.

THE EFFECT OF TEMPERATURE DROP AND TEMPERATURE LEVEL ON HEAT TRANSMISSION IN VERTICAL TUBE EVAPORATORS

By W. L. BADGER and P. W. SHEPARD

Read at the Montreal Meeting, June 28, 1920

THIS paper is the first contribution resulting from the work of the evaporator experiment station at the University of Michigan. It is expected that it will be followed at intervals by a series of similar papers, each one of which will be a contribution in itself, but all of which will ultimately bear on the general question of the transmission of heat from steam to water.

The experiments here reported cover determinations of heat transmission coefficients in a vertical-tube evaporator in three series, at boiling-points of 60°, 75°, and 100° respectively. In each series the boiling-point was kept constant and by varying steam temperature the mean temperature difference was varied. All known variables, other than temperature drop, were eliminated as far as possible so that the results are strictly comparable. Also, such conditions were chosen and such records taken that all these runs will be related to other investigations now in progress.

HISTORICAL

A qualitative discussion of the various factors affecting heat transmission from steam to water is given in so many places that it will not be taken up in this paper. The subject is treated by different authorities from different points of view, but the analysis by Claassen[1] seems to be the simplest and at the same time the most comprehensive. Claassen makes the following statement:

[1] Beet Sugar Manufacture, translated by Hall and Rolfe, 2d ed. (1910) p. 133–4.

" . . . the heat transference from steam to the boiling liquid is in proportion to:

" 1. The speed of the movement of the liquor over the heating surface;

" 2. Inversely as the height of the liquor, or its pressure, on the heating surface;

" 3. The speed with which the steam circulates over the heating surface;

" 4. The speed and thoroughness with which the condensed water is taken away from the heating surface:

" 5. The completeness of the vacuum in the evaporating-chamber;

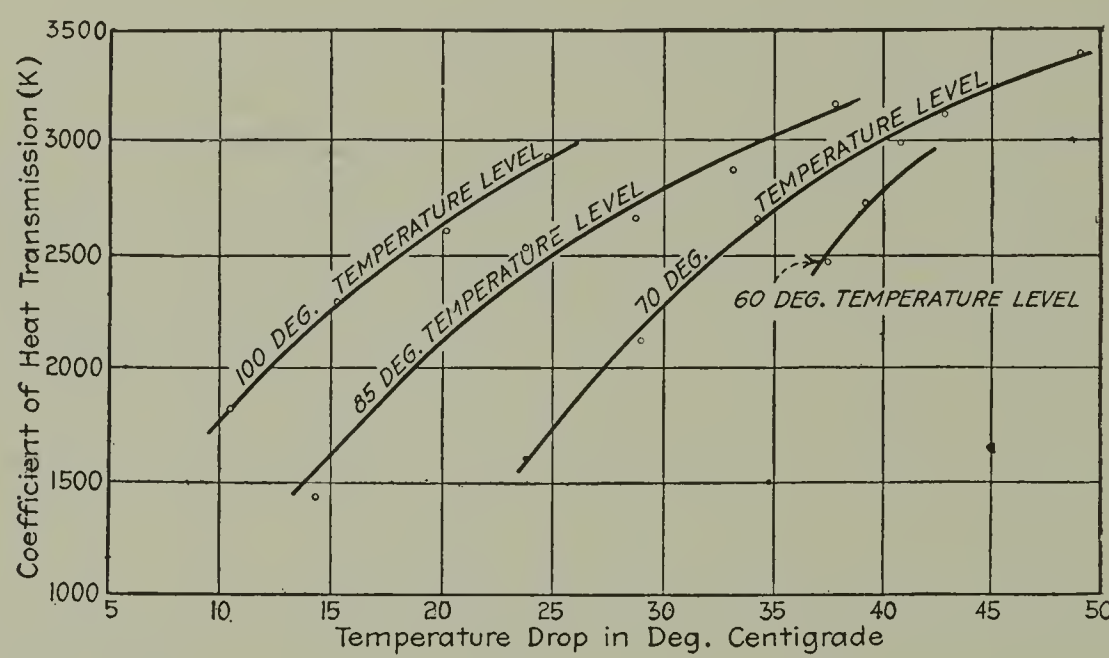

Fig. 1.—Effect of Temperature Level and Drop on Heat Transmission.

" 6. The conductivity of the heating surface, that is, its freedom from scale and foreign substance;

" 7. Inversely as the viscosity of the liquor;

" 8. The temperature of the liquor, which depends upon the pressure under which it boils;

" 9. The magnitude of the temperature-drop between the steam and the boiling liquor."

Claassen has investigated the effect of temperature-drop and temperature level on the coefficient of heat transmission on a laboratory scale.[1] The work was done in 1895. The experiments were made in a cylindrical vessel 19 inches in diameter and 46 inches high. The heating surface was a copper coil, 45 mm. ($1\frac{3}{4}$ inches) outside with a heating surface of 0.5 square meter (5.38 square feet). The whole

[1] Z. Ver. Zukerind., 52, 373.

apparatus stood on a scale. It was filled with water to a definite mark and a definite weight boiled off. The heat transmission was calculated on the amount of water evaporated and not on the amount of steam condensed. The temperature drop was the difference between the temperature of steam and of water as determined by mercury thermometers. The data in Claassen's article are too meager to permit recalculation to the true temperature drop (corrected for hydrostatic head). Claassen's results are therefore apparent conductivities.

Claassen's results are given in Table I and plotted in Fig. 1.

TABLE I

Heating Steam ° C.	Boiling-point ° C.	Temperature Drop. ° C.	K * ° C.
110.5	100.0	10.5	1823
115.3	100.0	15.3	2296
120.2	100.0	20.2	2611
124.8	100.0	24.8	2947
100.7	86.3	14.4	1435
109.9	86.1	23.8	2527
115.3	86.5	28.8	2672
119.7	86.5	33.2	2889
124.0	86.2	37.8	3185
100.0	71.0	29.0	2126
105.0	70.7	34.3	2670
110.2	69.4	40.8	3007
114.9	72.1	42.8	3140
119.5	70.4	49.1	3423
124.7	73.0	51.7	3619
98.0	60.5	37.5	2477
100.0	60.9	39.2	2741

* Throughout this paper thermal conductivities will be expressed as large calories per square meter per degree C. per hour and will be designated by K. The corresponding figure in English units (B.T.U. per square foot per degrees F. per hour) is usually designated by U. $U = 0.2048\,K$. Practically all work so far done is of such accuracy that simply dividing K by five will give U within the limits of error.

Claassen says: "These experiments show that within the limits of experimental error, the heat transmission coefficient increases with increasing temperature drop. This may be explained by the fact that circulation of the water is favorably affected by the increased number of steam bubbles, due to the higher temperature drop. The summary also shows that with equal temperature drops, the heat

transmission coefficient is greater the higher the temperature of the heating steam and the higher the temperature of the vapors or the boiling-point of the water. The explanation for this is readily understandable. At a lower boiling-point (which may be caused by decreased pressure in the boiling chamber), the vapors evolved occupy a larger volume and consequently continually cover, on the average, a larger part of the heating surface. At higher temperatures of heating steam, the heating steam is denser and can probably give up its heat more rapidly. But principally the increased temperature of the condensed water is of importance here since heat transmission from water to a heating surface proceeds noticeably faster at high temperatures."

Comparatively little attention apparently has been paid to Claassen's experiments, and most workers have continued to calculate heat transmissions on the basis of the idea that it was strictly proportional to temperature drop. Hausbrand[1] says: "The temperature of the heating steam must always be a few degrees higher than the boiling-point of the liquid evaporated. The greater the temperature difference between heating steam and the liquid the larger the amount of heat transmitted, and it is usually assumed (probably correctly) that the heat passing through unit surface in unit time is directly proportional to the temperature difference."

Hausbrand qualifies this, however, with the following statement: "It seems, however, that we may conclude from many observations that with increasing pressure of heating steam (which of course always brings a higher temperature) a certain increase is found in capacity calculated to one degree difference; this increased activity is not proportional to the temperature rise but seems to grow slower after passing certain temperatures.

"One reason for this phenomenon is probably to be found in increasingly more rapid movement of the liquid particles over the heating surface at higher temperatures. But this alone does not suffice for the explanation of the observation made so often of a great decrease in heat transmission at low pressures of heating steam (e.g., in multiple-effect evaporators) and its increase at elevated pressures."

Nowhere in his actual data or in his formulas does Hausbrand take further cognizance of this effect of varying temperature drop.

[1] Verdampfen, Kondensieren, und Kuhlen; 6th ed., 1918, p. 58.

Orrok [1] has shown that in surface condensers, heat transmission varies as $\frac{C}{\theta^{1/8}}$. This however, is of no significance as regards evaporators except by offering an example of heat transmission not directly proportional to temperature drop. Derr[2] states as the result of large-scale tests the rate of evaporation increases more rapidly than the temperature difference increases.

Kerr [3] studied this point to a certain extent. His experimental data, however, are not suitable for interpretation on this point, as his experiments involve too many variables. On page 34 he discusses this matter and cites a number of results from which he concludes that

$$U = 225 + 17500\,D$$

where D is the density of the heating steam in pounds per cubic foot. Orrok [4] has pointed out the great discrepancies in Kerr's work as reported. It will be noted that in Kerr's experiments, the effects of temperature difference and temperature level are confused. Kerr ran his experiments by varying the boiling-point and varying the steam pressure at the same time but so that, in general, the temperature difference was not constant. When the temperature difference was constant neither boiling-point nor temperature of heating steam was constant. Kerr plots his results in terms of steam temperature without taking cognizance of temperature level or temperature drop. The effect of these two factors is shown in this paper to be very considerable. Consequently no conclusions may be drawn from experiments where they are neglected.

Kerr has also reported [5] heat transmission coefficients from a large number of commercial evaporators operating under plant conditions. Here again, due to failure to compare those results which were obtained with the same temperature drop or with the same temperature level, his results are valueless in this present investigation, except as they show qualitatively an increase in heat transmission with increased temperature drop.

Kerr has endeavored to directly attack the question of relation

[1] Transactions A. S. M. E., 32, 1139.
[2] Hawaiian Sugar Planters Assn., Bull. No. 42; Int. Sugar J., 16, 471.
[3] Bull. No. 149, Louis. Agr. Experimental Station.
[4] Trans. Am. Inst. Mech. Eng., 38, 106.
[5] Transactions A. S. M. E., 38, 67.

between temperature drop and heat transmission.[1] He quotes six tests in which the temperature drop varied from 5.7 to 18.8° F., plots them, and says that they determine a horizontal line; i.e., that rate of heat transmission is independent of temperature drop. It should be noted, first, that the points plotted bear no resemblance to the numerical values in the table from which they are supposed to be taken; second, that the numerical values given in the table, when plotted, do not determine a straight line or any other curve, ranging among themselves by over 100%; and third, so small a range was covered by the experiments that they have no general significance.

It seems probably, in the light of the work reported in this paper, that if Kerr's results, both laboratory and plant tests, had been plotted in such a way as to eliminate variations in either temperature level or temperature drop, they might prove to be much more systematic than is apparent.

Description of Apparatus

The work reported in this paper was conducted in the vertical tube evaporator described in the previous paper.[2] The arrangement is shown in Fig. 2. The evaporator is 30 inches in diameter and the body measures 12 inches from bottom flange to cover flange. The steam basket is 16 inches outside diameter, 48 inches high and carries twenty-four 2-inch 13-gauge charcoal iron tubes, giving a heating surface of 6.315 square meters or 67.95 square feet. Steam is supplied through a 3-inch steam line and the condensate is removed from the steam basket by a 2-inch pipe. The evaporator was equipped with a round bottom throughout the course of the work. The various auxiliary apparatus is described in the paper previously mentioned, and the methods of measurement are discussed in detail later.

Test Operation

All experiments here reported were made on distilled water. The evaporator was started boiling and vacuum, steam pressure and feed were adjusted to their proper value. Care was taken to have this preliminary period last long enough so that all conditions became uniform and so that the steam basket and condensate receiver were

[1] Bull. La. Agr. Exp. Sta. No. 149, p. 41.

[2] Reference to description of laboratory.

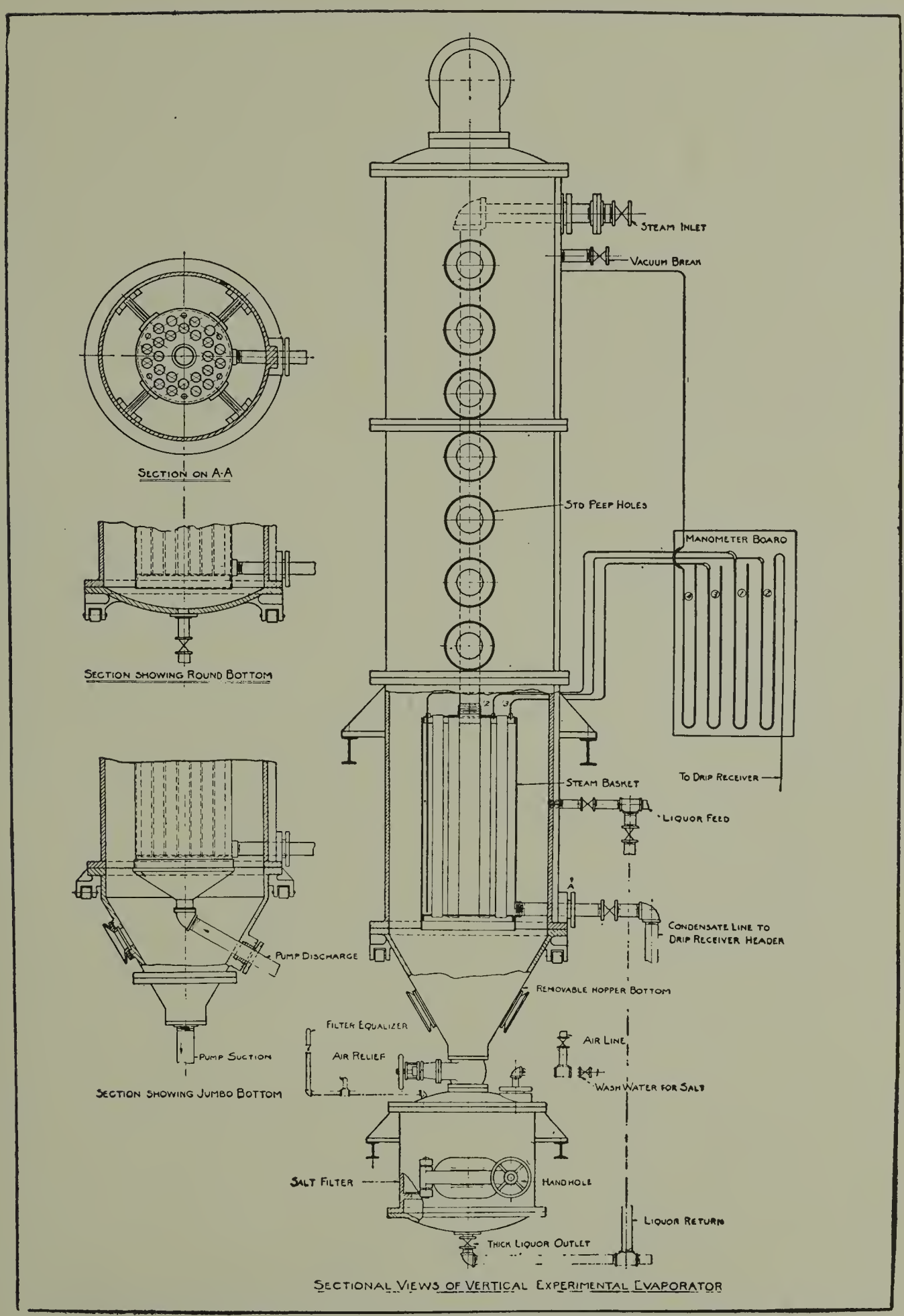

Fig. 2.—Diagrammatic Sketch of Vertical Tube Evaporator.

thoroughly vented of air. As a general thing one person operated the machine; one person recorded; and one person attended to feed supply, pumps, etc. When conditions were judged to be uniform a signal was given, the starting time was recorded and the level of condensate in the receiver was also noted. The desired temperatures and pressure readings were taken every two minutes during a run. Pressures were read to 1 mm. and temperatures were estimated to tenths of a degree. When a sufficient amount of condensed water had been obtained, at a signal from the recorder, the time was taken and the valve in the condensed water line closed. The vacuum was immediately broken and the evaporator shut down. This method was used during the early part of the work and is represented by such experiments as bear either a single number or a number followed by a letter only.

Later in the work a different method was adopted for ending the tests. When sufficient condensed water had collected, at a signal from the recorder the time and the level of the condensate were noted, but operation of the evaporator was not interfered with; the reading of time and condensate level for the end of one run being the readings for the beginning of the next run. Generally, however, the runs produced enough condensate so that at the end of one run, it was necessary to cut over into another condensate receiver; in which case a lapse of several minutes was allowed between the end of one run and the beginning of the next. The evaporator, however, was regulated as accurately as possible through this interval just as during the run proper. Where several runs were made in sequence without a shutdown of the evaporator, they are indicated by a number or a number and a letter followed by a dash and a Roman numeral.

Measurements

Level.—All these experiments were made with the water level even with the top tube sheet. In a few runs this level was regulated by hand. In such cases the distance of the water level above or below the reference point on the gauge glass was read every two minutes. The maximum variation with hand regulation was never more than 3 inches from the desired point, and the average variation for a run was less than one-half. In most of the runs a Tagliabue liquor level regulator was used. This kept the static level within $\frac{1}{2}$ inch of the desired point at all times. Even when boiling was so

violent that the liquid was splashing several feet into the air, sudden shut down of the machine showed that the static level was always still accurate. In another paper the effect of hydrostatic head is discussed; and it will be evident from the curves there shown that no appreciable error in the value from the heat transmission coefficient could result from such variations in liquor level as occurred.

Time.—An ordinary watch was used in determining the time of starting and stopping. It is believed that an error of not more than two seconds is the maximum under the conditions of operation. Since the majority of the runs were over twenty minutes long, this means that the error in determining the starting and stopping points of these experiments was of the order of 0.2%; and in most cases, considerably less than this.

Boiling Temperature.—The pressure in the vapor space was determined by a mercury manometer and regulated by the vacuum regulator described in the previous paper. The accuracy of regulation was variable, being much greater at the lower pressures. On the average, the variations from maximum to minimum seldom amounted to 10 mm. Since readings were taken every two minutes and since the runs were all over twenty minutes long, it will be seen that the average reading will have a probable error of considerably less than 1 mm. In the few cases where this probable error of the average was actually calculated, it was of the order of 0.01 mm. From tables of the vapor pressure of water, the temperature of the boiling liquid was calculated on the basis of this average pressure. An error of 1 mm. in the average pressure would make a difference of about 0.15 degree in the 60° series; about 0.08° in the 75° series; and 0.02° in the 100° series. It is believed that unknown errors could hardly result in an error of more than 2 mm. in this pressure. This would not amount to over 6% in the extreme case—the runs with 5° temperature drop at the 60° level.

Steam Temperature.—This is the point which caused the greatest difficulty and which is probably the cause for most of the variations noted in these experiments. A reference to Fig. 2 will show that for a number of feet the steam travels through a pipe entirely inside of the machine. Since it is the pressure and temperature of the steam in the steam basket which are of importance, measurements of these quantities outside the evaporator would be of no significance. It is obvious that direct-reading thermometers in the steam basket are impossible. At the beginning of this work considerable time was

spent in attempts to measure the steam temperature with thermocouples. This was a total failure due to the fact that if the thermocouples were protected, they were not sensitive enough; and if they were bare, their readings were complicated by galvanic E.M.F.'s. Preliminary work showed that they could not be relied on to as close as 1° C. Funds have not been available to provide a precision resistance thermometer which is probably the one way of measuring the steam temperature with sufficient accuracy.

The only method left was to measure the pressure of the steam and calculate its temperature from the steam tables. Seamless copper tubing was inserted into the steam basket through stuffing boxes, brought through the wall of the evaporator and connected to mercury manometers on the instrument board. One of these connections went just through the top of the steam basket; and one of them was carried to within 2 inches of the bottom of the basket. These two manometers never differed by more than 3 mm. and were usually much closer than that. The average of these manometer readings should be of the same order of accuracy as the average of the vacuum manometer discussed above and would give a correspondingly accurate value for the temperature of the steam, provided the steam contained no air and was not superheated.

At high steam pressures it was not possible to prevent the copper manometer lines filling with steam. The resulting condensation was very troublesome. So far as it resulted in water collecting in the manometers it could be allowed for. But there were always variations in readings in these cases which seemed to be due to water pockets in the tubing. This is the main reason for the small number of determinations at steam temperatures above 115°.

A small number of these experiments were made with low pressure from the university's mains, while the larger number were made with high-pressure steam which was throttled down to give the desired pressure in the steam basket. The fact that this high-pressure steam was generated largely from return water from the University's heating system means that it probably contained very little air. The 2-inch line from the steam basket to the condensate receiver was not filled by the amounts of water condensed in even the runs of highest capacity. A $\frac{1}{2}$-inch equalizer line from the drip receiver to the vapor space of the evaporator was always kept partly open. This resulted in a constant flow of steam and non-condensed gases from the basket to the drip receiver, and from the drip receiver to

the vapor space of the evaporator. In order to control this venting, another manometer (called the equalizer manometer) was installed. One side of this was connected to seamless copper tubing which ran into the top of the steam basket and down to within 2 inches of the bottom. The other side of the manometer was connected to the vent line a little above the top of the receivers. This manometer then showed the pressure drop between the bottom of the steam basket and the top of the drip receiver. The vent line from the drip receiver to the evaporator was throttled until this pressure drop was about 10 mm. of mercury. Comparative experiments showed that this was a much greater drop than necessary but this figure was used to be on the safe side. Since the steam basket used is comparatively long for its diameter, the non-condensed gases will be swept to the bottom and out through the condensate line. Therefore it is believed that the steam in the steam basket contained very little air. If we accept Orrok's conclusion for surface condensers, that the heat transmission coefficient decreases as the third power of the steam richness, 1% of air in the steam would cause a decrease in heat transmission of about 3%. In the case of those runs where the pressure in the basket was much below atmospheric pressure, there may have been this much air or more in the steam basket. The connections to the drip receivers are so complicated that there is a correspondingly large number of chances for air leaks; and the greatest difficulty was experienced in getting checks in the runs at highest vacua. Through most of the work, however, it is believed that less than 1% of air was present.

It is, however, quite certain that there was some superheat in the steam in a great many cases. The steam as it comes to the evaporator is wet, but since throttling at the regulating valve results in superheat, it has not been thought worth while to make moisture determinations on the part of the steam line which is available. To what extent moisture and superheat offset each other by the time the steam reaches the steam basket it is very difficult to say. Runs with the steam at about atmospheric pressure have shown no difference between the use of high-pressure steam throttled from 100 pounds down to atmospheric pressure on the one hand, and low-pressure steam with practically no throttling on the other hand.

Work on the horizontal tube evaporator, in cases where similar conditions of throttling existed, but where direct measurements of steam temperatures were possible, has shown about 10–15° of super-

heat when throttling to atmospheric pressure. This was in cases where steam flow was at about the same rate as the average rate in these tests. But in the horizontal evaporator the length of steam travel from the throttling valve to the heating surface is much shorter than in the vertical evaporator. Since the reaction between superheat and entrained water takes a measurable time, there is more chance of this equilibrium being reached in the vertical evaporator than in the horizontal. In order to determine the magnitude of the effect of superheat, let us assume a limiting case.

Let $t_1 = 150° =$ temperature of superheated steam at entrance of steam basket;

$t_s =$ temperature corresponding to pressure in steam basket;

$t_w = 75° =$ temperature of boiling water.

Then $\theta_a = t_1 - t_w = 75°$;

$\theta_e = t_s - t_w = 25°$;

$\theta_s = \dfrac{\theta_a - \theta_e}{\log_e \dfrac{\theta_a}{\theta_e}} =$ mean temperature difference during transfer of superheat;

$\theta_1 =$ mean temperature difference during transfer of latent heat

$\theta_s = \dfrac{75-25}{\log_e \frac{75}{25}} = 43.70°$;

$\theta_2 = t_s - t_w - 25°$.

Now if we weight these temperature drops in proportion to the amount of heat transmitted by each, we find that the general mean, θ_m, is

$$\frac{43.7 \times 24.2 - 25.0 \times 538.7}{24.2 - 538.7} = \frac{1058 - 13468}{562.9} = 25.8°.$$

The total heat transmitted is 4.5% too low if the superheat is neglected, and the temperature difference is 3% too low. These errors affect the result in opposite directions, so that the error in this case due to neglect of superheat would be negligible.

This does not take into consideration any difference between heat transmission from saturated and from superheated steam. It does not seem possible that as much as 50° superheat could exist; and unless due to the presence of superheat, there is a very great difference in the essential phenomena, it would seem that this error

is not enough to materially affect the results. Due to the pressure of other work, it has not been feasible to spend either the money or the time necessary to further investigate this point.

Weight and Temperature of Condensate.—In the condensate line immediately outside the evaporator a cross was placed. In the top opening of this cross was inserted a calibrated thermometer with its bulb dipping into a pocket formed by the plugged bottom outlet of the cross. The average of the readings of this thermometer is correct to less than one-tenth of a degree.

Two different procedures were followed in determining the amount of steam condensed. In the case of experiments where the condensed water was cooler than 100°, compressed air was turned into the drip receiver at the end of the test and the condensate blown out through a goose-neck into a weigh tank. Repeated trials of this method showed an accuracy always greater than 5 pounds. When the water was above 100° this method could not be used. In such cases the gauge glasses were read in mm. at the beginning and end of the test and the weight of water calculated from calibrations of the receivers. The temperature of the condensate was taken into consideration in making these calculations.

Temperature Difference.—The relation of the determination of steam temperature to temperature difference has been discussed above. Much thought was also given to the figure to be used for the temperature of the boiling water. Calibrated thermometers were inserted into the body at different points and their readings compared with those calculated from the vacuum as previously described. They differed between themselves by several tenths of a degree, and also from the temperature calculated from the vacuum. Because they were located in the descending current in the downtake and subject to radiation losses, it was felt that the temperature calculated from the vacuum was more reliable than any of them or than their average.

The effect of hydrostatic head is to increase the boiling-point in the lower layer of the liquid. The question also arose of correcting the boiling temperature for this. It was finally decided that the results would be most generally useful if calculated on the *apparent* temperature drop (temperature calculated from steam pressure less temperature calculated from vacuum). These are later corrected for hydrostatic head in a separate part of this paper. Where specific mention is not made to the contrary, *apparent* heat transmission

coefficients (i.e., calculated on the apparent temperature drop) are to be understood.

The effect of feed temperature is also to be considered. By reasoning similar to that employed in the case of the effect of superheat, it can be shown that the heat transmitted during heating is so small a part of the total heat transmitted that it would not affect the results if this heat were transmitted by a different temperature drop from that employed in the calculations. Further, it is questionable if cold feed ever gets to the layer next the heating surface where the heating is really done. Cold feed is probably heated by mixing with superheated lower layers, and from steam bubbles stirred in by the circulation.

Final Accuracy of Results.—When all the above measurements were considered it is seen that no one of them except the steam temperature will affect the temperature drop by more than 1%. There are of course, factors such as scale or rust on the heating surfaces, variations in circulation, and possibly others. It was found possible to obtain agreement between duplicates usually better than 5% but not always. What the absolute precision of the final results is would be very difficult to say; but the relative accuracy of the work may be judged better by the points on the curves than by numerical statements.

Calculation of Results

Pressures were measured in millimeters, temperatures in degrees C. and heat in kilogram calories. Where condensed water was weighed, it was weighed in pounds. When measured, it was calculated directly in kilograms. Heating surface was calculated on the basis of the wet surfaces. Both top and bottom tube sheets were included. The heating surface in tubes was 65.4% of the total, the rest being in the basket shell.

Heat input was taken as the sum of the latent heat at the temperature calculated from the pressure of the steam basket, and the sensible heat recovered between this temperature and the temperature of the condensate. All calculation from the simplest up were made independently by two different persons and checked back. All figures in the calculations were carried to 0.01° for temperatures; 0.1 mm. for pressures; 0.1 kg. for weights; and .01 cal. for heat. The final results were rounded off to the nearest even digit for K.

Results.

The essential data for the three series of experiments are given in tables II, III, and IV and in Fig. 3. It will be noted in the tables that the results are averaged in groups. In Fig. 3 the average of each group is indicated by a large circle. These circles have their centers at the exact points indicated in the averages and their radius in fifty units on the sacle for K. This is an arbitrary choice but is thought that it represents approximately the accuracy of the averages. At any rate there are few cases where it is possible to suppose that the average has a greater accuracy than this.

The principal thing which the curves indicate at once is the decided effect of both temperature level and temperature drop. The curves cannot be represented by a simple equation and it has not been thought worth while to try to derive any expression for them, in view of the limited significance of the absolute numerical values.

The large number of determinations on the 25° point on the 75° curve is due to the fact that this point is common to several sets of investigations now under way. The theoretical work of the station has been interrupted at numerous times. After each interruption this point was redetermined in order to be certain that the evaporator was in a condition similar to that under which the other runs had been made. No definite explanation can be made now for the fact that the 20° point on the 75° curve is low.

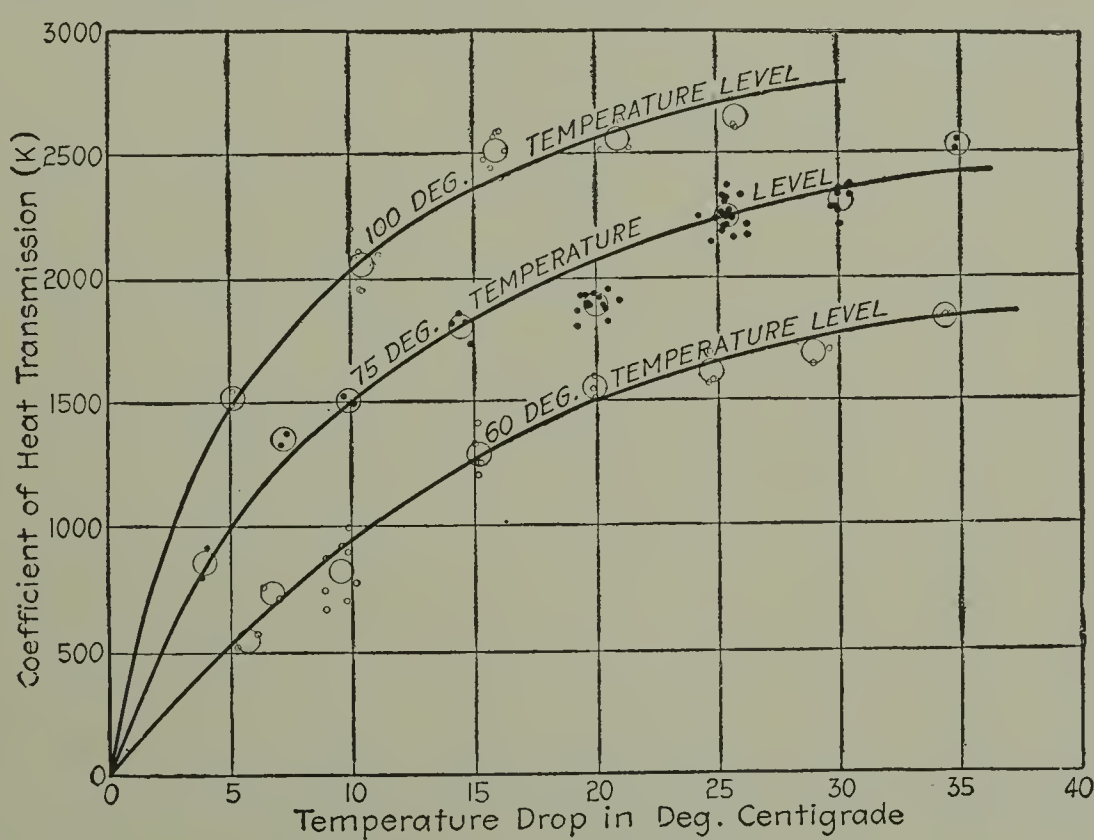

Fig. 3.—Relation between Apparent Heat Transmission, Coefficient and Temperature Drop for Different Boiling Points.

TABLE I

DATA OF INDIVIDUAL RUNS

Series.	Run No.	Level, Inches above Bottom Tube Sheet.	Time. Min.	Absolute Body Pressure p_v. mm. Hg.	Corres. Body Temp. t_w. C.°	Body Temp. from Thermometer. C.°	Absolute steam Pressure mm. Hg.	Corres. Steam Temp. t_s. C.°	Condensate Temperature. C.°	Condensate. Lbs.	Apparent Temp. Drop θ	Apparent K	U
A	50	4	50.33	285.4	74.69	73.88	769.1	100.33	93.47	309.0	25.64	873	178
A	47	6	36.42	286.2	74.74	75.46	762.0	100.07	96.14	695.0	25.33	2732	560
A	48	6	40.75	281.6	74.38	73.36	761.9	100.07	96.64	808.0	25.69	2796	573
A	49	6	37.80	283.5	74.54	72.46	767.2	100.26	96.57	716.0	25.72	2668	547
A	44	9	40.08	278.6	74.12	75.83	758.3	99.94	96.35	835.5	25.82	2925	599
A	45	9	35.75	280.1	74.26	73.28	764.6	100.17	96.73	708.0	25.91	2768	567
A	46	9	40.50	283.0	74.32	73.38	760.2	100.01	96.77	782.0	25.69	2722	558
A	40	12	39.75	270.4	73.42	72.84	761.5	100.06	94.80	776.0	26.64	2664	546
A	41	12	36.50	280.7	74.30	73.95	759.3	99.97	93.99	711.5	25.67	2763	566
A	42	12	38.75	280.4	74.27	72.95	762.3	100.08	95.91	764.0	25.81	2833	580
A	43	12	36.13	280.3	74.26	73.55	767.9	100.28	96.49	707.5	26.02	2724	558
A	36	18	48.25	282.0	74.40	74.07	764.8	100.18	94.47	807.5	25.78	2361	484
A	37	18	41.42	282.1	74.41	73.85	762.1	100.11	93.73	703.0	25.70	2405	493
A	38	18	47.42	286.1	74.89	74.07	759.4	99.98	94.35	790.0	25.09	2414	495
A	39	18	44.75	277.1	74.00	73.47	760.3	100.01	93.14	796.0	26.01	2494	511

TABLE I.—*Continued*

Series.	Run No.	Level, Inches above Bottom Tube Sheet.	Time. Min.	Absolute Body Pressure p_v. mm. Hg.	Corres. Body Temp. t_w. C.°	Body Temp. from Thermometer. C.°	Absolute steam Pressure mm. Hg.	Corres. Steam Temp. t_s. C.°	Condensate Temperature. C.°	Condensate. Lbs.	Apparent Temp. Drop θ	Apparent K	U
A	32	24	51.50	283.4	74.53	74.60	761.1	100.04	93.30	789.0	25.51	2192	449
A	33	24	50.75	285.1	74.65	74.91	760.3	100.01	92.41	768.5	25.36	2179	446
A	34	24	49.83	285.7	74.70	75.00	760.5	100.02	93.73	737.5	25.32	2129	436
A	35	24	45.75	285.8	74.71	74.79	758.8	99.96	94.36	693.5	25.25	2179	446
C	2B	24	31.75	282.7	74.47	74.99	762.4	100.09	88.94	474.0	25.62	2141	439
C	3B	24	30.83	282.6	74.47	74.92	760.9	100.03	88.63	467.5	25.56	2180	446
A	21	30	52.25	283.0	74.48	74.20	765.5	100.20	94.60	715.0	25.72	1935	396
A	22	30	50.00	279.4	74.18	74.30	765.2	100.19	93.10	692.5	26.02	1941	398
A	23	30	48.75	288.8	74.94	75.10	765.2	100.19	94.10	679.5	25.25	2008	412
A	24	30	57.33	287.6	74.85	75.00	765.6	100.21	94.50	776.0	25.36	1942	398
A	26	30	58.82	283.6	74.54	74.60	765.3	100.20	93.90	834.5	25.66	2012	412
A	27	30	61.33	285.9	74.72	74.70	761.8	100.07	92.90	860.0	45.25	2016	413
B	59	30	48.82	291.7	75.22	74.60	770.0	100.37	93.94	705.0	25.15	2109	432
B	69	30	60.83	294.1	75.47	74.93	770.5	100.38	94.58	878.5	24.97	2104	431
B	61	30	51.50	288.6	74.94	74.78	765.6	100.21	94.33	749.5	25.24	2098	430
B	62	30	51.17	287.3	74.86	74.66	764.1	100.13	94.17	723.5	25.29	2034	416
C	101	30	50.75	279.4	74.19	74.43	759.6	99.99	95.29	762.4	25.80	2114	433
C	102	30	46.25	276.6	73.96	73.73	754.5	99.79	95.46	680.5	25.83	2067	423
C	8A	30	37.00	285.5	74.82	74.76	759.6	99.98	89.61	558.5	25.16	2201	451
C	1B	30	33.92	282.6	74.76	74.97	762.0	100.07	87.03	498.5	25.61	2115	433

TABLE I.—*Continued*

Series.	Run No.	Level, Inches above Bottom Tube Sheet.	Time. Min.	Absolute Body Pressure p_v. mm. Hg.	Corres. Body Temp. t_w. C.°	Body Temp. from Thermometer. C.°	Absolute steam Pressure mm. Hg.	Corres. Steam Temp. t_s. C.°	Condensate Temperature C.°	Condensate. Lbs.	Apparent Temp. Drop θ	Apparent K	U
A	29	48	57.42	288.6	74.94	74.55	761.0	100.03	92.60	678.0	25.10	1720	352
A	30	48	61.42	276.3	73.93	73.13	765.5	100.20	92.55	796.5	26.27	1802	369
A	31	48	54.08	277.2	74.01	73.81	758.5	99.94	91.45	631.5	25.93	1620	332
B	51	48	60.41	286.4	74.78	74.71	671.1	100.04	95.13	781.5	25.26	1858	380
B	52	48	55.67	280.6	74.29	75.75	762.7	100.10	95.24	671.0	25.81	1696	347
B	55	48	50.53	280.2	74.26	74.17	762.1	100.08	94.58	629.5	25.82	1758	360
B	58	48	50.08	275.6	73.84	72.19	761.3	100.05	93.65	672.0	26.21	1905	390
C	5B	48	42.72	281.1	74.36	75.78	763.1	100.11	94.56	538.0	25.75	1778	364
C	6B	48	41.83	281.0	74.35	75.69	762.8	100.10	94.89	530.0	25.75	1787	366
B	53	60	65.75	277.9	74.04	75.42	763.8	100.14	95.35	695.0	26.07	1473	302
B	54	60	70.42	285.2	74.68	75.15	767.8	100.29	94.84	707.0	25.61	1425	292
C	7B	60	43.50	295.8	75.55	76.28	764.2	100.15	94.36	437.0	24.60	1486	304
C	8B	60	44.67	294.8	75.47	76.92	763.7	100.13	85.08	456.0	24.56	1539	315
B	56	72	65.75	278.9	74.15	72.78	764.3	100.16	93.74	617.5	26.01	1314	269
B	63	72	52.00	286.3	74.77	74.85	767.7	100.28	93.05	430.0	25.51	1182	240
B	64	84	71.33	279.6	74.21	75.12	767.3	100.27	94.48	525.0	26.06	1030	211
B	65	84	68.08	283.4	74.53	75.96	766.2	100.23	93.03	490.5	25.70	1022	209

TABLE I.—*Continued*

Series.	Run No.	Level, Inches above Bottom Tube Sheet.	Time. Min.	Absolute Body Pressure p_v. mm. Hg.	Corres. Body Temp. t_w. C.°	Body Temp. from Thermometer. C.°	Absolute steam Pressure mm. Hg.	Corres. Steam Temp. t_s. C.°	Condensate Temperature. C.°	Condensate. Lbs.	Apparent Temp. Drop θ	Apparent K.	U
C	22A	3	43.75	288.5	74.96	73.82	764.9	100.18	94.56	115.5	25.22	385	79
C	23A	3	41.00	288.4	74.95	72.30	761.0	100.04	93.64	110.0	25.09	390	80
C	10B	6	52.00	285.6	74.72	75.06	761.0	100.04	91.24	297.5	25.32	828	170
C	12B	6	52.67	287.4	74.87	75.68	764.9	100.18	94.64	302.0	25.31	824	167
C	13B	6	42.33	293.6	75.37	75.48	759.2	99.97	94.80	258.5	24.60	902	185
C	107	9	41.00	289.4	75.04	74.47	760.1	100.00	94.43	385.0	24.96	1369	280
C	108	9	42.33	281.9	74.31	73.41	756.4	99.87	94.35	450.5	25.56	1514	310
C	9B	12	40.82	277.5	74.03	73.85	763.3	100.12	95.36	632.5	26.09	2156	441
C	9A	12	32.00	286.8	74.57	74.09	764.1	100.15	86.37	306.5	25.58	2261	463
C	12A	12	30.75	295.9	75.56	74.04	767.5	100.27	95.66	451.5	24.71	2151	441
C	13A	12	51.75	299.1	75.82	73.84	763.0	100.11	95.34	742.0	24.29	2144	439
C	14A	12	40.58	274.6	73.78	72.48	764.3	100.16	95.55	676.0	26.38	2292	370
C	15A	12	50.33	283.3	74.57	73.98	762.8	100.10	95.72	808.0	25.53	2281	468
C	10A	18	32.25	284.0	74.58	74.82	765.8	100.21	86.19	506.5	25.63	2263	464
C	11A	18	33.83	280.8	74.31	74.91	760.3	100.01	87.20	520.0	25.70	2230	457
Average				283.9	74.57		763.3	100.11			25.54		

TABLE 1.—*Continued*

AVERAGES BY GROUPS

Series.	Level.	*K*	*U*
A	3	873	178
A	6	2732	560
A	9	2805	575
A	12	2746	562
A	18	2418	496
A–C	24	2167	444
A–B–C	30	2050	420
A–B–C	48	1769	362
B–C	60	1481	303
B	72	1248	254
B	84	1026	210
C	3	388	80
C	6	851	174
C	9	1442	295
C	12	2214	480
C	18	2246	460

TABLE II

DATA OF INDIVIDUAL RUNS, 60° TEMPERATURE LEVEL

I.	I.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Run No.	Time. Min.	Absolute Body Pressure P_v. mm. Hg	Corres. Body Temp. t_w. C.°	Absolute Steam Pressure. mm. Hg.	Corres. Steam Temp. t_s. C.°	Condensate Temp. C.°	Condensate. Lbs.	Apparent Temp. difference θ_1. C.°	K	U
183	60.0	145.9	59.56	186.2	64.87	64.39	68	5.31	516	104
44A	60.0	145.8	59.55	193.2	65.68	65.05	87	6.13	570	117
179 –II	60.0	134.8	57.88	186.8	64.93	64.75	125	7.05	713	153
181 –II	50.2	143.7	59.24	192.9	65.65	65.22	101	6.40	760	155
178 –II	15.25	136.1	58.08	216.5	68.26	67.02	164	10.18	773	158
178 –II	140.25	137.1	58.24	214.9	68.09	66.84	116	9.85	709	145
184	50.0	138.5	58.45	208.3	67.38	66.36	138	8.93	743	161
185	50.2	138.9	58.51	208.9	67.44	66.43	162	8.93	872	179
186	50.0	139.9	58.66	210.6	67.62	66.50	124	8.96	670	137
61B–I	42.5	138.6	58.47	217.2	68.34	65.81	157	9.87	899	183
61B–II	30.0	140.3	58.73	219.8	68.61	66.37	122	9.88	998	204
61B–III	30.0	140.2	58.71	216.7	68.28	65.28	110	9.57	922	189
50B–I	31.5	141.2	58.86	276.5	73.79	71.93	164	15.09	1334	273
50B–II	31.0	141.2	58.86	277.3	74.01	72.36	278	15.15	1417	290
177 –I	30.8	137.7	58.33	272.5	73.60	71.61	246	15.27	1254	257
177 –II	30.67	137.5	58.30	271.0	73.47	71.71	244	15.17	1260	258
177 –III	30.08	139.1	58.55	273.7	73.70	71.71	230	15.15	1208	248

TABLE II—*Continued*

I.	I.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Run No.	Time. Min.	Absolute Body Pressure P_b. mm. Hg.	Corres. Body Temp. t_w. C.°	Absolute Steam Pressure. mm. Hg.	Corres. Steam Temp. t_s. C.°	Condensate Temp. C.°	Condensate. Lbs.	Apparent Temp. difference θ. C.°	K	U
51B–I	30.0	145.5	59.51	347.1	79.43	76.51	401	19.92	1603	328
51BII	30.0	145.5	59.51	345.9	79.35	75.91	386	19.84	1551	318
51B–III	19.5	145.4	59.51	347.3	79.45	76.35	246	19.94	1514	310
52B–I	23.5	142.8	59.11	412.8	83.76	80.66	383	24.65	1573	322
52B–II	34.5	142.8	59.11	415.3	83.91	80.42	569	24.80	1583	324
52B–III	23.0	143.3	59.18	414.5	83.86	80.47	406	24.68	1701	348
175	23.75	139.5	58.45	488.2	88.05	84.10	506	29.60	1706	350
174	22.5	140.7	58.79	482.6	87.76	84.33	454	28.97	1650	333
53B–I	21.25	146.8	59.70	487.4	88.02	84.46	264	28.32	1736	356
176 –I	20.5	138.8	58.50	591.2	93.11	89.44	556	34.61	1847	378
176 –II	21.25	40.9	58.82	588.0	92.97	89.99	596	34.15	1847	378
178 –III	20.75	138.3	58.42	585.5	92.87	89.50	560	34.45	1847	378
Average of all runs.....		140.68	58.79							

TABLE II.—*Continued*

AVERAGE BY GROUPS

Steam Pressure. mm. Hg.	Steam Temp.[1] V.°	Steam Temp.[2] C.°	θ C.°	K	U
189.7	65.27	64.51	5.72	543	110
189.8	65.32	65.31	6.72	736	154
214.1	68.00	68.31	9.52	823	170
274.2	73.75	73.96	15.17	1295	265
346.8	79.41	78.69	19.90	1556	319
414.2	83.88	83.50	24.71	1619	331
486.0	87.94	87.75	28.96	1697	346
588.3	92.98	93.19	34.40	1847	378

[1] Average from data of Column VI.
[2] Average of Column IV + average from data of Column IX.

TABLE III

DATA OF INDIVIDUAL RUNS, 75° TEMPERATURE LEVELS

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Run No.	Time. Min.	Absolute Body Pressure P_v. mm. Hg.	Corres. Body Temp. t_w. C.°	Absolute Steam Pressure. mm. Hg.	Corres. Steam Temp. t_s. C.°	Condensate Temp. C.°	Condensate. Lbs.	Apparent Temp. difference θ. C.°	K	U
46B–I.	54.0	288.6	74.97	338.1	78.79	77.78	69	3.82	797	163
46B–II.	54.0	287.8	74.90	340.7	78.98	78.14	85	4.08	919	188
172	61.0	286.6	74.80	386.0	82.07	80.89	256	7.27	1374	281
173 –II.	60.0	290.0	75.08	387.2	82.15	81.09	222	7.07	1333	254
38A–I.	29.0	283.7	74.55	427.0	84.61	82.38	184	10.06	1497	306
38A–II.	29.75	289.8	75.06	427.6	84.67	83.11	184	9.61	1525	412
47B–I.	29.75	285.6	74.72	508.2	89.11	86.05	336	14.37	1856	380
47B–II.	30.5	290.8	75.15	510.4	89.22	86.26	330	14.07	1820	373
48B–I.	32.75	289.2	75.02	519.2	89.67	87.27	371	14.65	1824	374
48B–II.	31.5	289.6	75.06	523.8	89.90	86.74	343	14.84	1733	355
193 I.	27.0	283.9	74.60	632.0	94.93	93.96	440	20.33	1877	384
193 –II.	40.0	282.9	74.51	632.8	94.96	94.09	640	20.45	1829	374
195 –I.	30.0	286.6	74.82	651.6	95.74	95.79	514	20.92	1911	392
198 –I	30.0	283.4	74.55	634.2	95.02	91.65	512	20.47	1958	401
198 –II.	30.0	285.4	74.72	633.6	95.0	91.43	489	20.28	1890	387
205 –I.	24.5	288.6	74.96	631.0	94.86	92.04	402	19.90	1938	397
205 II.	24.0	288.8	75.0	636.0	95.10	92.0	395	20.10	1920	393
208 –III.	26.5	289.6	75.07	625.7	94.66	92.63	427	19.59	1930	395
208 –IV.	24.5	289.4	75.05	626.4	94.69	92.34	386	19.65	1884	386
208 –V.	24.5	291.2	75.20	631.4	94.90	92.43	389	19.72	1891	387
39A–I.	33.0	285.3	74.69	618.7	94.34	91.64	524	19.65	1898	345
39A–II.	33.5	290.0	75.11	621.2	94.45	91.29	532	19.34	1930	395
39A–III.	30.0	291.6	75.24	621.0	94.44	91.15	443	19.20	1808	370
39A–IV.	33.5	292.3	75.27	623.0	94.52	91.43	512	19.25	1864	382

208 –I.	23.0	292.4	75.30	765.5	100.20	98.56	552	24.90	3345	460
208 –II.	24.5	292.3	75.29	761.1	100.04	98.03	558	24.75	2145	439
207 –I.	31.0	286.5	74.81	762.9	100.11	98.05	754	25.30	2242	458
207 –II.	25.0	288.0	74.94	761.6	100.06	97.84	590	25.12	2189	448
207–III.	25.5	284.3	74.63	767.4	100.27	97.94	607	25.64	2166	444
209 –II.	30.0	277.6	74.06	767.4	100.27	97.85	734	26.21	2175	446
209 –III.	23.0	281.8	74.42	776.5	100.60	98.59	573	26.18	2218	454
41B–II.	28.5	297.9	75.72	756.7	99.90	97.00	664	24.18	2249	446
41B–III.	23.9	286.7	74.78	760.2	100.01	96.80	583	25.23	2257	465
41B–IV.	26.25	287.0	74.83	760.4	100.02	97.10	661	26.19	2335	476
60 –I.	19.5	293.2	75.35	781.8	100.79	96.67	484	25.44	2278	466
60B–II.	20.2	290.0	75.09	767.8	100.28	96.28	480	25.19	2207	452
60B–III.	19.5	290.0	75.09	733.2	100.48	96.87	479	25.39	2260	463
187	25.0	280.7	74.33	766.9	100.25	98.54	651	25.92	2339	479
188	27.0	283.4	74.55	762.8	100.10	97.58	664	25.55	2243	459
190 –II.	26.5	284.8	74.67	760.9	100.03	98.67	672	25.36	2325	477
190 –III.	22.0	286.1	74.78	761.4	100.05	98.84	552	25.27	2310	473
190 –IV.	28.0	285.9	75.76	762.2	100.08	99.10	714	25.32	2375	486
197 –I.	29.5	286.6	74.82	763.7	100.13	96.94	708	25.31	2213	453
197 II.	30.0	287.1	74.87	759.2	99.97	96.70	731	25.10	2268	464
201 –I.	24.0	293.3	75.35	916.4	105.32	102.50	729	29.97	2340	479
201 –II.	24.0	292.5	75.31	916.0	105.31	102.33	734	30.00	2364	484
192 –I.	16.0	283.9	74.60	906.7	105.02	104.26	502	30.42	2384	488
192 –II.	23.0	284.7	74.66	906.6	105.02	104.85	720	30.36	2379	487
192 –III.	22.0	283.8	74.59	905.7	104.99	104.41	676	30.40	2338	479
49B–I.	26.25	282.5	74.45	889.2	104.45	100.51	752	30.00	2222	455
49B–II.	26.25	283.5	74.54	889.6	104.46	101.22	744	29.92	2290	469
49B–III.	26.0	283.2	74.51	890.6	104.50	100.98	762	29.99	2273	466
49B–IV.	26.0	287.9	74.91	892.8	104.57	101.30	760	29.66	2291	469
204 –I.	20.0	289.3	75.04	1065.8	109.76	106.80	759	34.72	2521	516
204 –II.	19.0	290.4	75.14	1074.0	109.99	107.30	736	34.85	2564	525
Average of all runs.....		287.6	74.89							

TABLE III.—*Continued*

AVERAGES BY GROUPS

Absolute Steam Pressure mm. Hg.	Steam Temp.[1] C.°	Steam Temp.[2] C.°	θ C.°	K	U
339.4	78.88	78.84	3.95	858	176
386.6	82.11	82.06	7.17	1354	277
427.3	84.64	84.73	9.84	1511	309
515.4	89.48	89.38	14.49	1808	370
629.9	94.83	94.81	19.92	1895	388
763.0	100.18	100.22	25.33	2252	468
901.5	104.85	104.97	30.08	2302	475
1069.9	109.88	109.97	34.78	2542	520

[1] Average from data of Column VI.
[2] Average of Column IV + average from data of Column IX.

TABLE IV

DATA FOR INDIVIDUAL RUNS 100° TEMPERATURE LEVEL

I.	I.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Run No.	Time. Min.	Absolute Body Pressure P_v. mm. Hg.	Corres. Body Temp. t_w. C.°	Absolute Steam Pressure. mm. Hg.	Corres. Steam Temp. t_s. C.°	Condensate Temp. C.°	Condensate. Lbs.	Apparent Temp. difference θ. C.°	K	U
63B–I.	30.0	738.4	99.19	881.9	104.22	102.17	97	5.03	1491	305
63B–II.	30.0	738.4	99.19	881.7	104.21	102.41	100	5.02	1547	317
65B–I.	20.0	735.3	99.08	1049.8	109.31	106.04	177	10.23	1998	419
65B–II.	21.75	735.3	99.08	1049.9	109.31	106.88	204	10.23	2110	432
65B–III.	19.0	735.3	99.08	1042.2	109.10	105.72	172	10.02	2088	428
212 –III.	18.0	736.7	99.14	1039.4	109.02	107.41	170	9.88	2203	451
215 –I.	16.0	731.3	98.93	1972.5	109.95	107.69	160	11.02	2097	429
215 –III.	16.0	731.3	98.93	1064.9	109.73	107.53	154	10.80	2052	420
45A–I.	30.0	733.3	99.00	1048.3	109.26	105.95	260	10.26	1955	399
45A–II.	29.15	733.3	99.00	1051.9	109.37	106.30	256	10.36	1954	398
210 –I.	29.50	745.9	99.48	1288.2	115.48	113.72	533	16.01	2590	530
210 –II.	29.0	745.9	99.48	1280.2	115.29	113.79	536	15.81	2660	545
210 –III.	29.0	745.9	99.48	1282.0	115.34	113.56	522	15.86	2588	530
211 –I	24.0	738.2	99.19	1285.0	115.41	113.59	428	16.22	2512	514
213 –I.	21.0	731.1	98.92	1254.6	114.67	112.20	370	15.73	2568	526
213 –II.	28.0	731.1	98.92	1238.3	114.27	112.43	465	15.55	2477	507
216 –I.	16.0	733.2	99.00	1268.0	115.00	112.91	267	16.00	2384	488
216 –II.	17.5	733.2	99.00	1270.3	115.08	112.90	295	16.06	2404	492
216 –III.	16.0	733.2	99.0	1253.0	114.66	112.31	267	15.66	2444	500
64B–II.	20.0	738.4	99.19	1458.1	119.34	115.77	445	20.15	2520	516
214 –I.	26.0	729.3	98.85	1489.6	120.17	117.74	616	21.32	2526	518
214 –II.	25.0	729.3	98.85	1481.9	119.83	117.90	532	20.98	2634	538
191 –I.	18.0	744.4	99.42	1741.7	125.02	124.04	557	25.60	2726	558
191 –II.	22.0	744.9	99.44	1743.5	125.06	124.09	656	25.62	2621	537
191 –III.	25.0	745.9	99.46	1749.3	125.16	124.39	745	25.70	2613	535
Average of all runs.....		736.7	99.13							

TABLE IV.—*Continue*

AVERAGES BY GROUPS

Absolute Steam Pressure mm. Hg.	Steam Temp.[1] C.°	Steam Temp.[2] C.°	θ C.°	K	U
881.8	104.21	104.13	5.02	1519	311
1052.4	109.38	109.46	10.25	2057	422
1268.8	115.02	114.97	15.86	2514	515
1476.5	119.78	119.93	20.82	2560	524
1744.8	125.08	124.75	25.64	2653	543

[1] Average from data of Column VI.
[2] Average of Column IV + average from data of Column IX.

TABLE V

Mean values at intervals of 5° temperature drops, corrected for hydrostatic head; 60° temperature level series.

Average body temperature at top tube sheet for whole series..... 58.79° C.

Average body temperature at bottom tube sheet for whole series..... 69.59° C.

θ_1	t_s	θ_2	θ_{mh}	Apparent. K	Corrected. K
5	63.79	0.0	2.50	525	1050
10	86.79	0.0	5.00	940	1880
15	73.79	4.20	9.60	1270	1984
20	78.79	9.20	14.60	1500	2054
25	83.79	14.20	19.60	1660	2117
30	88.79	19.20	24.60	1770	2159
35	93.79	24.20	29.60	1850	2188

Where $\theta_1 = 5.0°$, K corrected for both hydrostatic head and inactive heating surface = 2563.

Where $\theta_1 = 10.0°$, K corrected for both hydrostatic head and inactive heating surface = 2134.

TABLE VI

Mean values at intervals of 5° temperature drops, corrected for hydrostatic head: 75° temperature level series.

Average body temperature at top tube sheet for whole series..... 74.89° C.

Average body temperature at bottom tube sheet for whole series..... 81.37° C.

θ_1	t_s	θ_2	θ_{mh}	Apparent. K	Corrected. K
5°	79.89	0.0	2.50	1005	2010
10°	84.89	3.52	6.76	1515	2246
15°	89.89	8.52	11.76	1840	2346
20°	94.89	13.52	16.76	2070	2470
25°	99.89	18.52	21.76	2240	2573
30°	104.89	23.52	26.76	2365	2640
35°	109.89	28.52	31.76	2435	2684

Where $\theta_1 = 5.0°$, K corrected for both hydrostatic head and inactive heating surface = 2750.

TABLE VII

Mean values at intervals of 5° temperature drop, corrected for hydrostatic head; 100° temperature level series.

Average body temperature at top tube sheet for whole series..... 99.13° C.

Average body temperature at bottom tube sheet for whole series.....192.23° C.

θ_1.	t_s.	θ_2.	θ_{mh}.	Apparent. K	Corrected. K
5	104.13	1.90	3.45	1490	2160
10	109.13	6.90	8.45	2050	2426
15	114.13	11.90	13.45	2370	2643
20	119.13	16.90	18.45	2570	2786
25	124.13	21.90	23.45	2710	2890
30	129.13	26.90	28.45	2800	2952

Corrections for Hydrostatic Head.

In order to get a basis for more general comparisons, these figures were all corrected for hydrostatic head. The points corrected were not the average actually determined but were read off the smooth curves. The method of recalculation is illustrated by the following example:

Let t_s = temperature of steam (calculated from pressure);
t_w = temperature of boiling liquid at the surface (calculated from vacuum);
t_b = temperature of boiling liquid at the bottom tube sheet;
$\theta_1 = t_s - t_w$ = temperature difference at surface = "apparent" temperature drop;
$\theta = t_b - t_s$ = temperature difference at bottom;
$\theta_{mh} = \frac{\theta_1 \times \theta_2}{2}$ = mean temperature difference corrected for hydrostatic head;
P_v = absolute pressure in vapor space;
P_h = head of liquid on bottom tube sheet in millimeters mercury.
$P_b = P_v + P_h$ = total pressure at bottom tube sheet.

For example, take the 25° point on the 75° curve.

$$P_v = 287.6 \text{ mm. } t_w = 74.89°;$$
$$t_s = t_w + 25.00° = 99.89°;$$
$$\theta_1 = 25.00°.$$

The hydrostatic head is 48 inches of water at a temperature of about 75° (sp. gr. of water at 75° = 0.9749).

$$P_h = \frac{48 \times 25.4}{13.6} \times 0.9749 = 87.4 \text{ mm.};$$

$$P_b = 287.6 + 87.4 = 375.0 \text{ mm.}, \; t_b = 81.37°;$$

$$\theta_2 = 99.89 - 81.37 = 18.52°;$$

$$\theta_{mh} = \frac{18.52 + 25.00}{2} = 21.76°.$$

Now from the curve we read the apparent K at $\theta = 25.0°$ as 2240. Then the corrected K is $2240 \times \frac{25.00}{21.76} = 2573$ cal. The complete data from such calculations are given in tables V, VI, and VII and are

plotted in Fig. 4, to which the curves for apparent K are added for comparison.

This method of calculation calls for boiling-points higher than steam temperature for the 5° and 10° points on the 60° curve and for the 5° point on the 75° curve. These cases were handled as follows: The point on the basket where the boiling-point of the liquid should become equal to the temperature of the steam was determined. At this point, then, the true temperature difference should be zero so far as any boiling is concerned. The mean temperature difference over the part of the heating surface used for

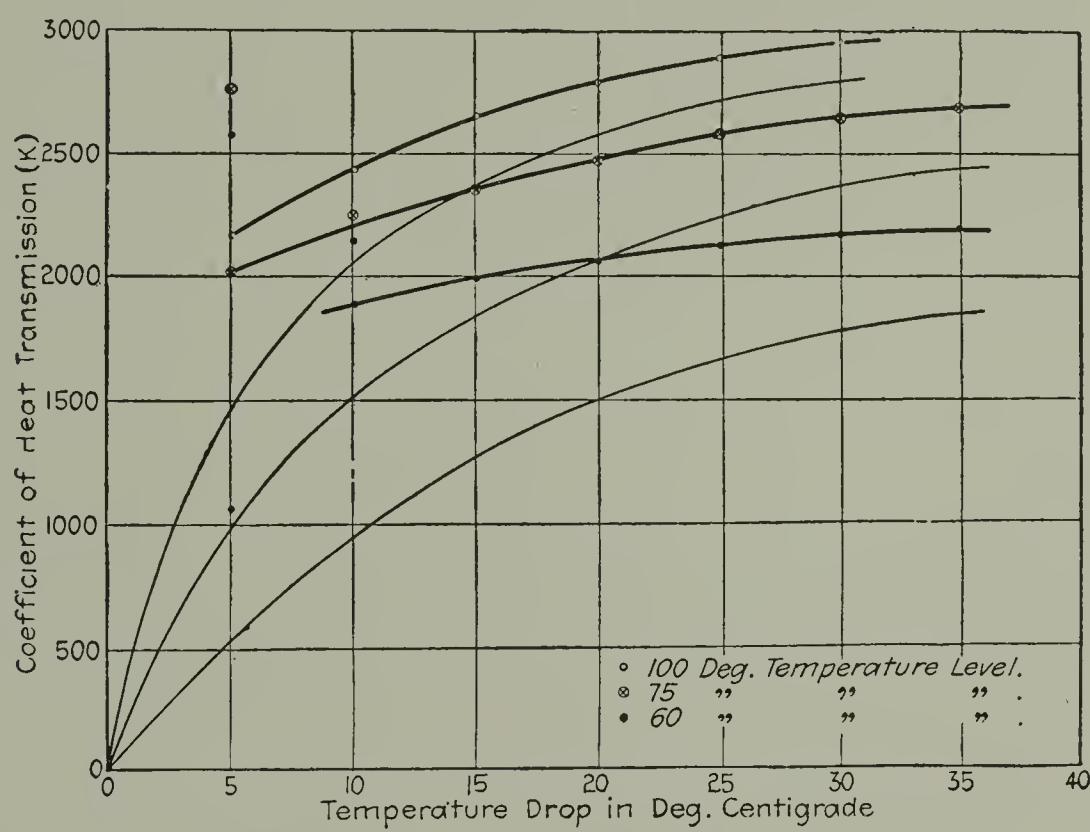

FIG. 4.—Data of Fig. 3. Corrected for hydrostatic head.

boiling was taken as the arithmetical mean of zero and the temperature difference at the top. Assuming that the heating surface below this point was totally inactive, the apparent values for K were recalculated on the basis of the new temperature drop and the diminished heating surface. For the sake of comparison, this correction was also made on the basis of temperature drop only, neglecting any consideration of decreased heating surface. Both values so obtained are plotted for each of the three points in question.

It will be seen that neither assumption was correct but that the truth lies somewhere between the two. The values calculated on the basis of no action in the lower part of the heating surface

are too high; thus showing that there is some heat transmitted below the point where theoretically there is no temperature difference between boiling liquid and steam. On the other hand heat transmission in this area cannot be as high as during boiling, for the values calculated on the basis of the whole heating surface are far too low. Evidently then, there is some action in the lower part of the basket in heating liquid from the temperature in the downtake (which is that corresponding to the vacuum, or a little below because of radiation and incoming feed) to temperatures approaching steam temperature. Since heat transmission from steam to non-boiling water is known to be at a far lower rate than heat transmission from steam to boiling water, this furnishes a qualitative explanation for the difference in results from the two assumptions. It has not been considered worth while to try to draw any quantitative results from these considerations.

It should be noted that the corrected coefficients change very little with change in temperature drop. What slope these lines do have is undoubtedly due to the factor of increased circulation pointed out by Claassen (see page 103 above). It will also be noted that these corrected curves differ from each other nearly as much with changes in boiling-point as do the apparent values for K. Many reasons for this will suggest themselves such as increased density of steam, decreased viscosity of boiling liquid, decreased viscosity (and consequently better drainage) of condensed water, better thermal conductivity of condensed water, etc. The authors at present have no definite explanation to offer as to the cause of this increase in heat transmission with increase in boiling-point.

Another interesting fact is that at higher temperature levels both the apparent and the corrected curves are becoming parallel.

The hydrostatic head corrections furnish a ready explanation for the fact that the apparent values for K approach zero as the temperature drop approaches zero.

As the apparent temperature drop (θ_1) approaches zero, this means that t_w approaches t_s. As t_w approaches t_s, the distance below the top tube sheet where $t_b = t_s$ approaches zero. Hence the inactive part of the heating surface approaches the whole heating surface, and the total heat transmitted approaches zero. But since in calculating the apparent heat transmission coefficient the whole heating surface is used, it is evident that the coefficient must therefore also approach zero as the heat transmitted decreases.

Relation of Steam Temperature to Heat Transmission

If a section is taken across the curves of Fig. 3 at right angles to the X-axis, one obtains a curve showing the combined effect of increased steam temperature and increased boiling-point for the same

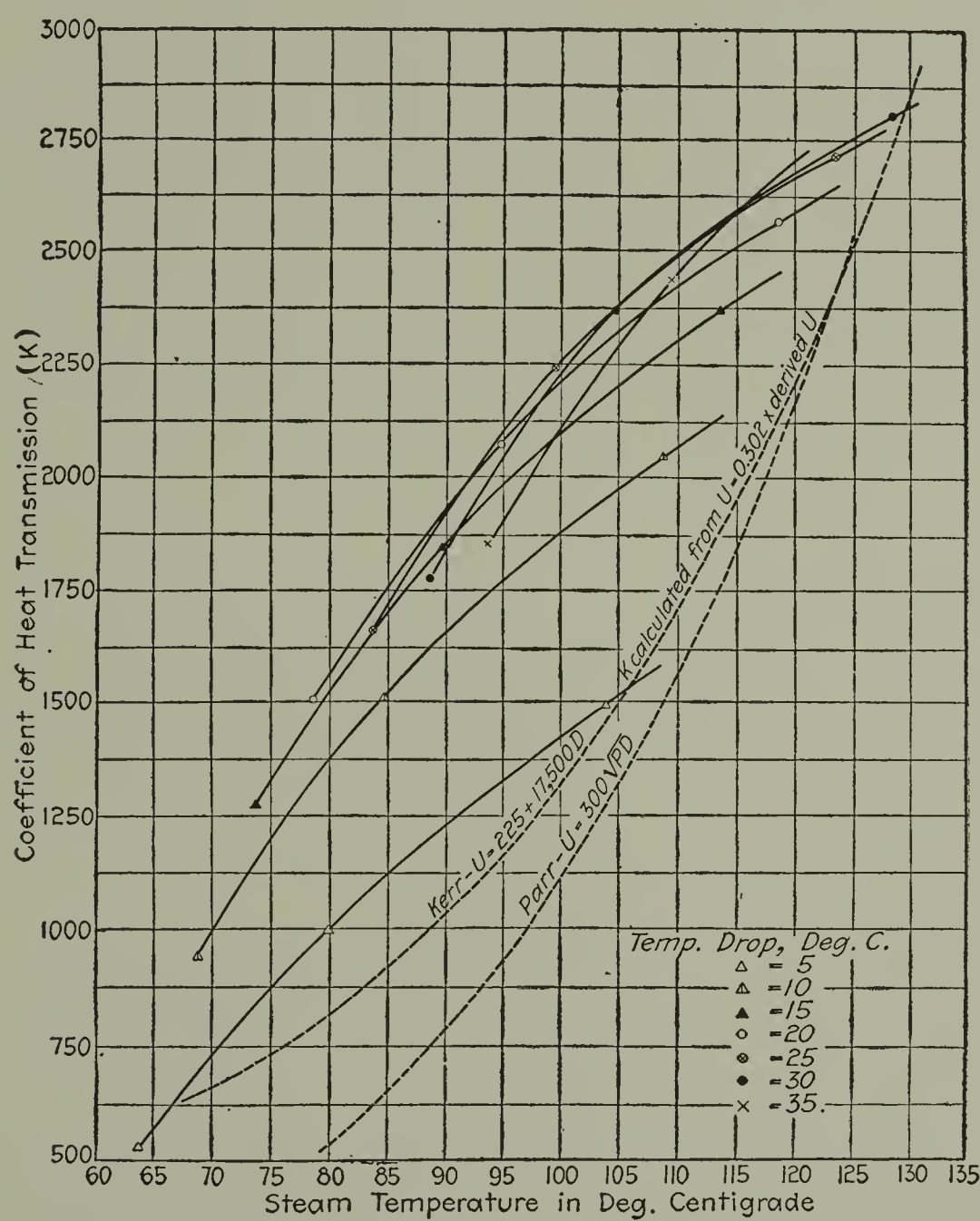

Fig. 5.—Variations in Heat Transmission with Steam Temperature, for Various Temperature Drops.

temperature drop. Such sections taken for temperature drops in multiples of 5° are plotted in Fig. 5. These curves are obviously developing a fairly definite limiting curve to the left, but will extend out to fill the whole space to the right. Fig. 5 furnishes an excellent explanation for the very wide variations in Kerr's results both experi-

mental[1] and on the commercial scale.[2] Kerr plots K against steam temperature without any regard to temperature drop and then attempts to derive a single equation to cover all these points. Our results show how completely false it is to assume such an expression.

On the basis of his experimental results, Kerr develops an equation, $U = 225 + 17.500\ D$, where D = steam density in pounds per cubic foot. In attempting to plot this equation in Fig. 5, it was found that the equation called for such high values of K that they came entirely off our chart. To make Kerr's figure for steam at 130° check with our figure for steam at 130° and the 30° temperature drop, his results as calculated and converted to metric units are multiplied by 0.302. The resulting values are plotted in Fig. 5.

Parr[3] has suggested for multiple effect evaporators, $U = 300\sqrt{PD}$, where P is the absolute pressure of the heating steam in pounds per square inch, and D is the density of steam in pounds per cubic foot. Parr's equation is derived from theoretical considerations and not from experimental data. Values calculated from this expression and converted to metric units are also plotted in Fig. 5. These results and those of Kerr are reproduced here merely to illustrate how impossible it is to represent heat transmission over a range of values for either boiling-point, steam temperature, or temperature drop, by any expression which does not involve at least two of these three factors.

It will be seen by a comparison of the corrected values for K and the apparent values for K, that one part of the cause for low coefficients in the latter bodies of multiple-effect evaporators is accounted for by the effect of hydrostatic head. Of the many factors which affect heat transmission coefficients, hydrostatic head is the one which is susceptible of calculation. The authors believe that if values reported in the literature for heat transmission coefficients had been uniformly corrected for hydrostatic head, the results would be found much more concurrent and systematic than they have been thought to be. As work progresses in the evaporator experiment station and more data are accumulated on both apparent and corrected heat transmission coefficients over a wider range of conditions, it seems not unreasonable to expect that the choice of the coefficient for the different bodies of the multiple effect may not be

[1] Bull. No. 149, La. Agr. Exp. Sta., p. 33.
[2] Trans. A. I. M. E., 30, 67.
[3] Engineering, 121, 146.

such difficult matter in the end. Removing the factor of hydrostatic head may remove much of the uncertainty regarding heat transmission coefficients at low boiling temperatures or low temperature drops.

Conclusions

The following conclusions for the present must be taken as indicating tendencies only and must be applied with caution for evaporators which differ very much in design from the evaporator in which they were determined.

1. The apparent coefficient of heat transmission in vertical tube evaporators decreases in temperature drop and approaches zero for zero temperature drop.

2. The apparent coefficient of heat transmission increases with boiling-point for a given temperature drop (which also means increasing steam temperature).

3. Correcting the apparent heat transmission coefficients for hydrostatic head gives figures which change but little with temperature drop. This remaining change is probably due to increased circulation at increased rates of boiling.

4. The corrected heat transmission coefficients used show considerable differences as the boiling-point is increased and the temperature drop held constant.

5. It is impossible to represent heat transmission coefficients for different boiling points, different temperature drops and different steam temperatures by an expression which does not consider at least two of these three factors.

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STUDIES IN EVAPORATOR DESIGN. II.

THE EFEECT OF HYDROSTATIC HEAD ON HEAT TRANSMISSION IN VERTICAL TUBE EVAPORATORS

By W. L. BADGER and P. W. SHEPARD

Read at the Montreal Meeting, June 28, 1920

General.—This paper reports a series of determinations of heat transmission in an experimental vertical tube evaporator, to show the effect of hydrostatic head (and incidentally the effect of the shape of the bottom of the evaporator) on this constant. This investigation was undertaken in the Evaporator Experiment Station of the University of Michigan as a part of the general program of the study and correlation of all the factors and variables affecting heat transmission in evaporators. It was felt that since our general problem involved a quantitative study of evaporators on a larger sacle, over wider ranges, and with a different disposal of heating surface than any investigator has hitherto attempted as a research proposition, it would be well to risk the possible repetition of some of the work already done.

Historical.—Claassen very early pointed out the fact that increasing the hydrostatic head on a surface must result in a decrease in heat transmission. He carried out some experiments [1] in a small experimental evaporator which has been described in a previous paper.[2] His experiments on this subject are only four in number and the actual hydrostatic head is not recorded. The experiments with "high" hydrostatic heads show a heat transmission about 5% lower than those with "low" hydrostatic heads.

Hausbrand [3] omits entirely the discussion of this point with reference to heat transmission.

Kerr [4] has studied this point and has given several curves showing

[1] Z. Ver. Zuckerind., **52**, 373.

[2] Page 101.

[3] Verdampfen Kondensieren und Kuhlen, 6th ed., 1918.

[4] Bull. 149, Louis. Agri. Experiment Station.

the effect of hydrostatic head on heat transmission. He shows that the maximum heat transmission occurs when the tubes are about one-third submerged; that the decrease in heat transmission at higher levels than this approximately follows a straight line; and that this decrease is greater than the decrease calculated from the increased pressure. In other places in the literature [1] are found the statements that vertical tube evaporators give the maximum heat transmission when the tubes are about one-third submerged.

Apparatus.—The experiments here described were run in the vertical tube evaporator at the evaporator experiment station of the University of Michigan. This apparatus has been previously described.[2] The steam basket employed in these runs contains twenty-four 2-inch 13-gauge charcoal-iron tubes, 30 inches long. These experiments are divided into three series corresponding to different arrangements of the evaporator. In series (*A*) the body of the evaporator from bottom flange to top flange was 8 feet high and the evaporator was equipped with a round bottom. In series (*B*) an intermediate section was added so that the body of the evaporator was 12 feet high, but otherwise the same as in series (*A*). Series (*C*) was also run with the body 12 feet high but a 60° cone bottom was substituted for the round bottom of the previous tests.

Method of Manipulation and Accuracy of Results.—These have been discussed in a previous paper and this discussion need not be repeated here.

Results.—The results are given in Tables I,[3] II, and III, and in Plate I. At levels about 24 inches, all the results at a point were averaged. At levels below 24 inches, the results when the round bottom was used are averaged separately from the results with the cone bottom. In all runs the liquor level averaged less than $\frac{1}{2}$ inch from the desired point. Consequently all the individual results obtained at each level should be in a single vertical line. They are spread sideways a little to make it possible to distinguish individual determinations. There are several interesting features in this curve.

It will be noted that with the round bottom, the maximum heat transmission occurs at exactly one-third submergence. This confirms the results of other investigators. It will also be noticed that

[1] Webre, J. Ind. Eng. Chem., **10**, 191; Rousseau, Trans. A. S. M. E., **38**, 109.

[2] See page 77.

[3] See page 116.

TABLE II

HYDROSTATIC HEAD CORRECTION FOR LEVELS BELOW TOP TUBE SHEET

Average apparent temperature drop for all series (θ_1) = 25.54°C
Average body pressure for all series (p_v) = 283.9 mm.
Corresponding temperature (t_w) = 74.57°C
Average steam temperature for all series (t_s) = 100.11°C

Series.		A	A	A	A	A	A+C	C	C	C	C
Level—inches above bottom tube sheet		3	6	9	12	18	24	6	9	12	18
Heating surface above liquor level	H_a	3.540	3.161	2.779	2.401	1.643	0.882	3.161	2.779	2.401	1.643
Heating surface below liquor level	H_b	0.533	0.912	1.294	1.672	2.430	3.191	0.912	1.294	1.672	2.430
Hydrostatic head on bottom tube sheet	p_h	5.5	10.9	16.4	21.8	33.8	43.6	10.9	16.4	21.8	32.8
Total pressure on bottom	p_b	289.4	294.8	300.3	305.8	316.7	327.6	294.8	300.3	305.8	316.7
Temperature at bottom	t_b	75.03	75.49	75.94	76.37	77.22	78.05	75.49	75.94	76.37	77.22
Temperature drop at bottom	θ_2	25.09	24.62	24.17	23.74	22.89	22.06	24.62	24.17	23.74	24.20
Mean weighted temperature difference	θ_{mh}	25.51	25.43	25.32	25.16	24.74	24.12	25.43	25.32	25.16	24.74
Apparent K		873	2732	2805	2746	2418	2167	851	1442	2214	2246
Corrected K		875	2741	2830	2787	2495	2293	854	1453	2247	2317

at levels higher than the top tube sheet, heat transmission decreases with increase in level along a straight line; but this relation does not hold between the top tube sheet and the maximum.

TABLE III

HYDROSTATIC HEAD CORRECTIONS FOR LEVELS ABOVE TOP TUBE SHEET

Average apparent temperature drop for all series (θ_1) = 25.54.°C.
Average body pressure for all series (p_v) = 283.9 mm.
Corresponding temperature (t_w) = 74.57°C.
Average steam temperature for all series (t_s) = 100.11°C.

Series		A+B	A+B	B	B	B
Level, inches above bottom tube sheet		30	48	60	72	84
Hydrostatic head on top tube sheet, mm	p_h[1]	0.0	32.8	54.6	76.5	98.3
Total pressure on top tube sheet.....	p_t	283.9	316.7	338.5	360.4	382.2
Boiling temperature at top tube sheet..	t_t	74.57	77.22	78.84	80.38	81.84
Temperature drop at top tube sheet..	θ_3	25.54	22.89	21.27	19.73	18.27
Hydrostatic head on bottom tube sheet	p_h	54.6	87.4	109.2	131.1	152.9
Total pressure on bottom tube sheet..	p_b	338.5	371.3	393.2	415.0	436.9
Boiling temp. at bottom tube sheet....	t_b	78.84	81.12	82.55	83.91	85.22
Temperature drop at bottom tube sheet	θ_2	21.27	18.99	17.56	16.20	14.89
Mean temperature drop.....	θ_{mh}	23.40	20.94	19.42	17.96	16.58
Apparent K.....		2050	1705	1475	1248	1026
Corrected K.....		2236	2065	1940	1776	1579

The point of greatest significance is the difference in the shape of these curves, due to the shape of the bottom of the evaporator. The explanation for this difference is fairly obvious. As will be shown later, although these curves show the change in heat transmission as the liquor level is varied, this change is really due largely to changes in circulation and only to a small extent to changes in hydrostatic head. The round bottom contains a comparatively small amount of liquid in proportion to the amount above the bottom tube sheet and therefore circulation of the entire mass is very vigorous. The cone bottom contains a large mass of liquid which absorbs energy of circulation in eddy currents. With low liquor levels, the proportion of liquid in the cone to liquid above the bottom tube sheet is large and therefore the effect of the cone is marked. As the liquor level rises, the proportion of liquid in the cone becomes less,

so that at levels approximately at the top tube sheet, it has no effect on the general circulation.

The bearing of this relation on the design of evaporators is obvious. A hopper bottom is used on a vertical tube evaporator when the formation of crystals or precipitates is expected. But under these circumstances it is comparatively rare that a vertical tube evaporator would be operated at low liquor levels because of the danger of building up deposits on the heating surface. When an evaporator is run as salting evaporators usually are, with the liquor level at the top tube sheet, the effect of the cone bottom disappears. On the other hand, in evaporators for liquid which can be boiled at low liquor levels, it is of importance to keep the volume of liquid below the bottom tube sheet as small as possible.

To determine how much of the effect shown by these curves is actually caused by hydrostatic head, points were read off the curves as plotted and recalculated to actual conductivities as follows:

Let t_s = temperature of heating steam (calculated from pressure);
t_w = temperature of the boiling liquid at its surface (calculated from the vacuum);
t_b = temperature of the boiling liquid at the bottom tube sheet;
t_t = temperature of the boiling liquid at the top tube sheet;
$\theta_1 = t_s - t_w$ = temperature difference at the surface (apparent temperature difference);
$\theta_2 = t_s - t_b$ = temperature difference at the bottom tube sheet, corrected for hydrostatic head;
$\theta_3 = t_s - t_t$ = temperature difference at the top tube sheet, corrected for hydrostatic head;
θ_{mh} = mean weighted temperature difference, corrected for hydrostatic head;
p_v = absolute pressure in the vapor in millimeters mercury.
p_h = head of liquid on the bottom tube sheet, millimeters mercury;
$p^1{}_h$ = head of liquid on the top tube sheet, millimeters mercury;
$p_b = p_v + p_h$ = total pressure at the bottom tube sheet in millimeters mercury;
$p_t = p_v + p^1{}_h$ = total pressure at the top tube sheet, millimeters mercury;
H_a = heating surface above liquor level, square millimeters;
H_b = heating surface below liquor level, square millimeters;

Then to illustrate the derivation of the values in Table II, for hydrostatic heads below the tube sheet, the following computation is given:

$$p_t = p_v = 283.9;$$
$$p_b = p_v + p_h = 283.9 + 43.6 = 327.5;$$
$$t_t = t_w = 74.57°;$$
$$t_b = 78.05°;$$
$$\theta_1 = \theta_3 = t_s - t_w = 100.11 - 74.57 = 25.54°;$$
$$\theta_2 = t_s - t_b = 100.11 - 78.05 = 22.96°;$$
$$\theta_{mh} = \frac{\theta_2 H_b + \theta_1 H_a}{H_a + H_b} = \frac{(22.06 \times 3.191) + (25.54 \times 0.882)}{4.073} = 24.12°.$$

Then the corrected $K = \frac{\theta}{\theta_{mh}}$ (apparent K) $= \frac{(25.54)}{(24.12)}\ 2167 = 2293.$

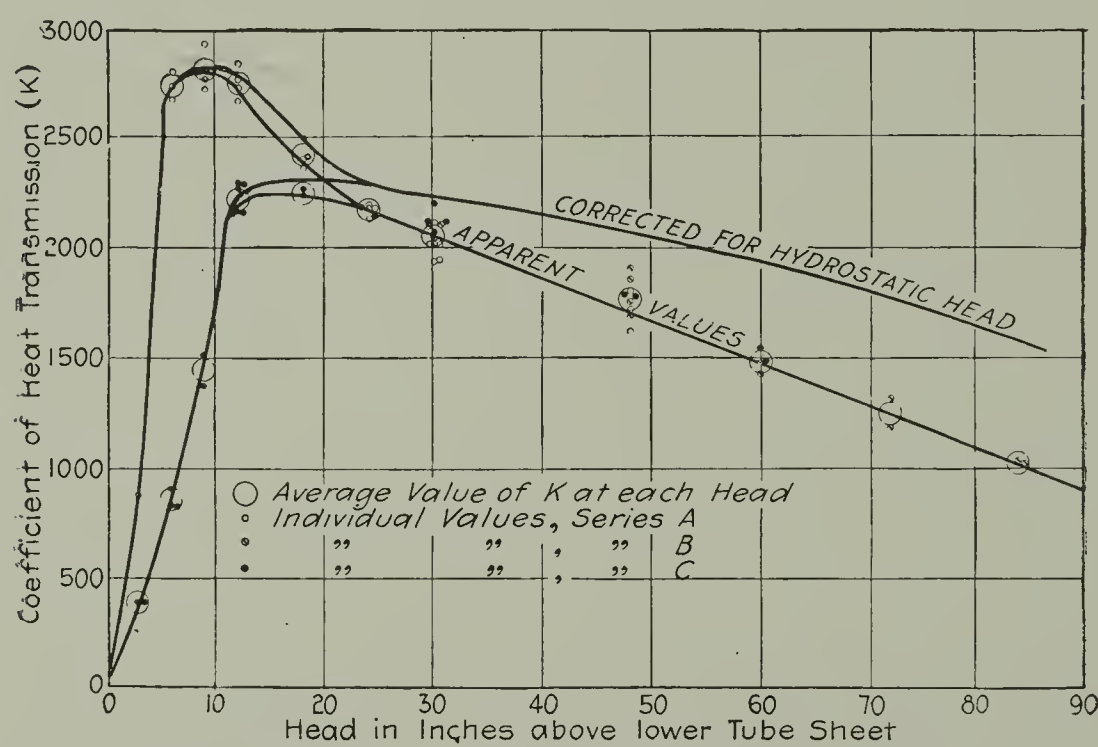


FIG. 1.—Variation of Heat Transmission with Head.

In taking θ_{mh} as the arithmetical mean the assumption has been made, to simplify calculation, that the boiling-point of water is a linear function of the hydrostatic head. This is, of course, not so, but for want of a simple equation expressing the relationship, the above approximation is taken as true enough for our purpose.

The results are connected by the curve indicated in Fig. 1. Evidently the effect of hydrostatic head is subordinate to the effect of velocity of circulation. More detailed discussion of the effect of velocity is unprofitable until a considerable number of similar curves under different conditions of operation have been determined.

It should be emphasized that the elevation in boiling-point, due

to increased hydrostatic head, is not shown by a thermometer immersed in the lower part of the boiling liquid. In an evaporator of the type here used, where the descending circulation is in the outer annular down-take space, a thermometer inserted into this annular space should always read a temperature corresponding to the vacuum or a little lower. The liquid in this down-take space is coming from the upper part of the evaporator where it has lost any superheat it may have had, and must enter the down-take either at the temperature corresponding to the vacuum or at a lower temperature if it cools by radiation.

If the columns showing temperature calculated from vacuum and temperature of body are compared, it will be seen that the temperature read by the thermometer tends to be lower than that calculated from the vacuum at low liquor levels and higher than that calculated from vacuum at high liquor levels. This thermometer was situated not far from the feed inlet and consequently at low liquor levels (which mean high rates of evaporation and consequently high rates of feed in proportion to the total amount of liquid in the evaporator) it gives a low reading, due to currents of colder feed liquor. Through the middle of the range where the effect of feed is less and yet circulation is strong, the two temperatures agree fairly well. At very high liquor levels, there is very little real circulation, but rather an agitation or bouncing. This bouncing may at times result in some superheated liquid from the lower part of the steam basket being carried up into the annular space as far as the thermometer bulb. At ordinary levels and with ordinary circulation there will be no appreciable elevation of the general temperature of the boiling liquid.

Conclusions.—The following conclusions must be for the present considered as indicating tendencies only; and should be applied with caution to evaporators which differ very much in design from the evaporator in which they were determined.

1. The maximum heat transmission when boiling water or other non-foaming, non-viscous materials in a vertical tube evaporator occurs when the tubes are from one-third to one-half submerged.

2. The position of this maximum point and its value depends on the size and shape of the evaporator bottom. With bottoms containing little liquid below the bottom tube sheet, the maximum occurs at lower levels and has a higher value than with bottoms containing large amounts of liquid.

3. Differences in the shape of the bottom have little effect on

heat transmission when the amount of liquid in the evaporator above the bottom tube sheet is larger than the amount of liquid below the bottom tube sheet.

4. As the liquor level is increased above the top tube sheet, the heat transmission falls off along a straight line.

5. The change in heat transmission with changing liquor level is only partially due to the effect of hydrostatic head. Changes in velocity of circulation are a very important factor.

All the work of this paper was done with funds supplied by the Swenson Evaporator Company, to whom the authors wish to express their indebtedness for permission to publish these results.

Evaporator Experiment Station,
Chemical Engineering Department,
University of Michigan,
Ann Arbor, Mich.

DISCUSSION

Vice-President Howard: This paper is now open for discussion.

Mr. Moore: Mr. Badger has left us up in the air in one part of his talk. He speaks of the temperature drop and the rate of heat transmission in the temperature drop as not varying with the degree, but actually being greater because of the temperature drop. Now, as a matter of fact, the reason for that is because of the greater mobility of the liquor and the greater velocity. Certainly the liquor must be taken into consideration, and you will get the very same curve that you will get by plotting the greater temperature drop.

There is another thing which is a small matter, but in order to be absolutely correct, when you plot the static head against guage pounds, a point halfway down the tube would not represent actual or mean difference of temperature, but for some purposes it will be near enough as he spoke of it. I just correct that because I know he did not mean to give the impression that it was exactly at that point. But it was such a highly scientific article that I did not want him to give the impression that that was it.

I wish to bear out his statement in relation to the nature of the material which you conduct through. There are many condensers which figure so many feet of copper at 500 B.T.U. conductivity per square foot, and so many feet of iron at 233 a square foot, and

so on. Now, as a matter of fact, the whole thing depends not upon the subject of the material—the lead or copper or iron, within certain limits that will all come together at about 1400 B.T.U. per square foot. And I think that if Mr. Badger carried his experiment up to high velocity he would have found that all the curves of these metals would come together.

Mr. Badger: If I could do the various things which I would like to do, to make this paper complete, it would be about 15 years work ahead. I have so many things of that kind that Mr. Moore has suggested that I don't know when I can get it tied down. The remarks about the temperature drop are correct if referred to the curve for hydrostatic head. That I know is due to the inceased velocity and increased mobility but the other matter is due to hydrostatic head. I do believe with Mr. Moore that if we could measure the velocity and correct for variations in velocity, we would find that our heat transmission coefficients expressed in terms of temperature drops, would be flat lines and that it affects heat transmission only as it affects the velocity. I am glad you pointed out the matter of the mean point of the tube not being the correct point. That is correct, and although in our calculations we so used it, we did so consciously because one could not get that mean point without a very complex investigation which we did not undertake to carry through. It introduces an error, but I am glad that the point was made so that it will be understood that we did not neglect it.

Vice-President Howard: I would like to ask Mr. Badger if he made any experiments with the Lilly Evaporator.

Mr. Badger: No, sir, the published tests on the Lilly Evaporator are confined entirely to Professor Kerr's work, and he plots his results without any attention being paid to the boiling point or the temperature drop, and therefore it is very difficult to interpret his results and to know with what others to compare them. It is similar to the point Mr. Moore made in the comparison of the electrolytic cells. You can take two cells, one in its worst state and one in its best state and get exactly the opposite from the correct effect. And since I do not know how Mr. Kerr made his determination, I cannot say whether the Lilly is better or worse.

Mr. Durfee: I would like to ask Mr. Badger under what condition this increase to 15 per cent in copper was made; whether the tubes were cleaned or scalded.

Mr. Badger: I should say that that figure of 15 per cent is not taken from experimental work in our laboratory but is an average figure taken from several different experiments in other places. It is not a figure which I can back up. It is in that order of magnitude, but I have made no determinations myself.

Vice-President Howard: Are there any further questions?

Mr. Zeisberg: Mr. Badger has pointed out a co-operation with industry on the part of his University which we are all very glad to see, and he has pointed out also how this particular effort is partially financed by those directly concerned. I should like to inquire what arrangements exist for making the facilities of that laboratory generally available to manufacturers who want to use them.

Mr. Badger: Under the contract between the Swenson Evaporator Co. and the Board of Regents it is provided that, once installed, the title of the machinery and equipment passes to the University and is available for any purpose which the University may have in mind, such as instruction, research, demonstration, etc. It is also provided that in return for the gift, the Swenson Evaporator Co. may do work, the results of which will remain its property or the property of its clients. Thus it will be seen that there are two methods whereby others could make use of this equipment—first, through the University, and, second, through the Swenson Evaporator Co.

In the past the University has had no organization by which it could handle work for others, except as advanced students might hold fellowships from outside concerns, or work on problems suggested by outsiders as a matter of general interest. At the present time, however, we have under consideration a Department of Engineering Research. This has been approved by the University, but it is not fully organized as yet. It is to be a department through which consultation and research problems of certain types can be brought to the University and assigned to members of the staff of the College of Engineering. Hence, if there were problems on which the equipment of the Evaporator Experiment Station might be used, the problem might be brought to the Department of Industrial Research, who would decide whether or not it was a suitable problem to be undertaken at the Evaporator Experiment Station, how it would be financed, and what would be the arrangement regarding ownership and publicity of results.

The other method would, of course, be to bring the problem to the Swenson Evaporator Co. and have them take it up through their rights in the Evaporator Experiment Station; in which case the work would be subject to the contract between the Swenson Evaporator Co. and the Board of Regents.

The problem of ownership of results was naturally a delicate one, since it involved a state university. The general principle which is expressed in the contract between the Swenson Evaporator Co. and the Board of Regents is approximately to this effect: That whenever the Swenson Evaporator Co. bears all of the expense of the investigation and everything connected therewith, the information remains their private property; unless that information happens to be a discovery of a general fundamental and scientific principle, in which case it is to be public property, no matter how the investigation was financed. It is quite probable that contracts made by the Department of Engineering Research will be based on the same idea.

STUDIES IN EVAPORATOR DESIGN. III.

BOILING POINTS OF SALT SOLUTIONS

By W. L. BADGER and E. M. BAKER

Read at the Montreal Meeting, June 28, 1920

As a part of the extensive program of research, undertaken in the Evaporator Experiment Station of the University of Michigan, on heat transmission in evaporators and the various factors affecting evaporator design, a study is being made of the loss in effective temperature drop between heating steam and boiling liquid, due to excess boiling point of the solution being evaporated. To this end it has been found necessary to attempt to collect all possible data on vapor pressure-temperature curves at varying concentrations of the more important chemicals recovered from solution in the industries, and where information is not available or is of doubtful value, to determine the necessary data in this laboratory. This paper particularly concerns an investigation of such curves for sodium chloride, and a critical review of such data contained in the literature.

In the design of an evaporator installation, it is necessary to know the " excess boiling point " of the solution being evaporated in each effect, at the temperature and pressure existing in that effect, in order to be able to calculate the heating surface required in any given case. This so-called " excess boiling point " is merely the elevation of the boiling point of the solution over the boiling point of pure water at the given pressure. The difference between the temperature of the steam supplied to the evaporator, t_1, and the temperature of the vapor coming from the solution t_2, may be divided into three parts:

a. Loss of effective temperature drop due to the excess boiling point of the solution.

b. Loss of effective temperature drop due to the effect of hydrostatic head.

c. Temperature drop available to cause heat transference from the steam to the boiling solution.

Hence, the available or effective temperature drop may be much less than the total temperature drop, since $c=(t_1-t_2)-(a+b)$. For example, a saturated solution of NaCl will boil at 108.7° C. under a pressure of 760 mm. mercury, while water boils at 100° C. If steam at 115° C. were used to cause evaporation of water, and also of a saturated NaCl solution, in evaporators operating under 760 mm. pressure, there would be an effective temperature drop (neglecting for the moment the hydrostatic head losses) across the heating surface of only 6.3° C. in the case of the salt solution, as compared with 15° C. in the case of water or a solution that does not have an excess boiling point. Moreover, the heat transmission per degree temperature drop per square meter of heating surface will be much less the smaller the temperature drop.[1] The excess boiling point represents a loss of temperature drop, which means loss of evaporator *capacity*, not of thermal efficiency of the set of pans.

While the literature shows a large number of determinations of elevation of the boiling points of aqueous solutions, many of these are for dilute or only moderately concentrated solutions, or are at atmospheric pressures. On critical examination, many of the values given are found to differ widely. Hence this laboratory has undertaken the rather ambitious program of examining the values given in the literature, and of making such determinations as may be necessary to prepare tables of sufficient range and accuracy for the purpose of evaporator design.

The first problem to be studied has been the excess boiling point of sodium chloride solutions. This was taken up with the intention of later testing our theories by actual tests on salt pans regularly in operation.

It should be pointed out here that it is impractical to calculate elevation of boiling point or depression of vapor pressure from the physico-chemical considerations. Many of the laws, as Raoult's, hold rigidly only for ideal solutions. Equations and formulæ have however been advanced which attempt to take into consideration all the factors involved, but these, at least from the engineering standpoint, are impracticable. It is evident that for exact application of such formulæ a knowledge of the degree of dissociation of the solute and of association of the molecules and ions of the solute with the solvent must be known over the entire range of concentrations

[1] See Studies in Evap. Design, I. The relation of temperature drop and temperature level to heat transference in the vertical tube evaporator.

and pressures. Much of the theoretical work has attempted to establish a quantitative relationship between the boiling points of solutions and osmotic pressure. Some excellent work of Dr. Orin E.

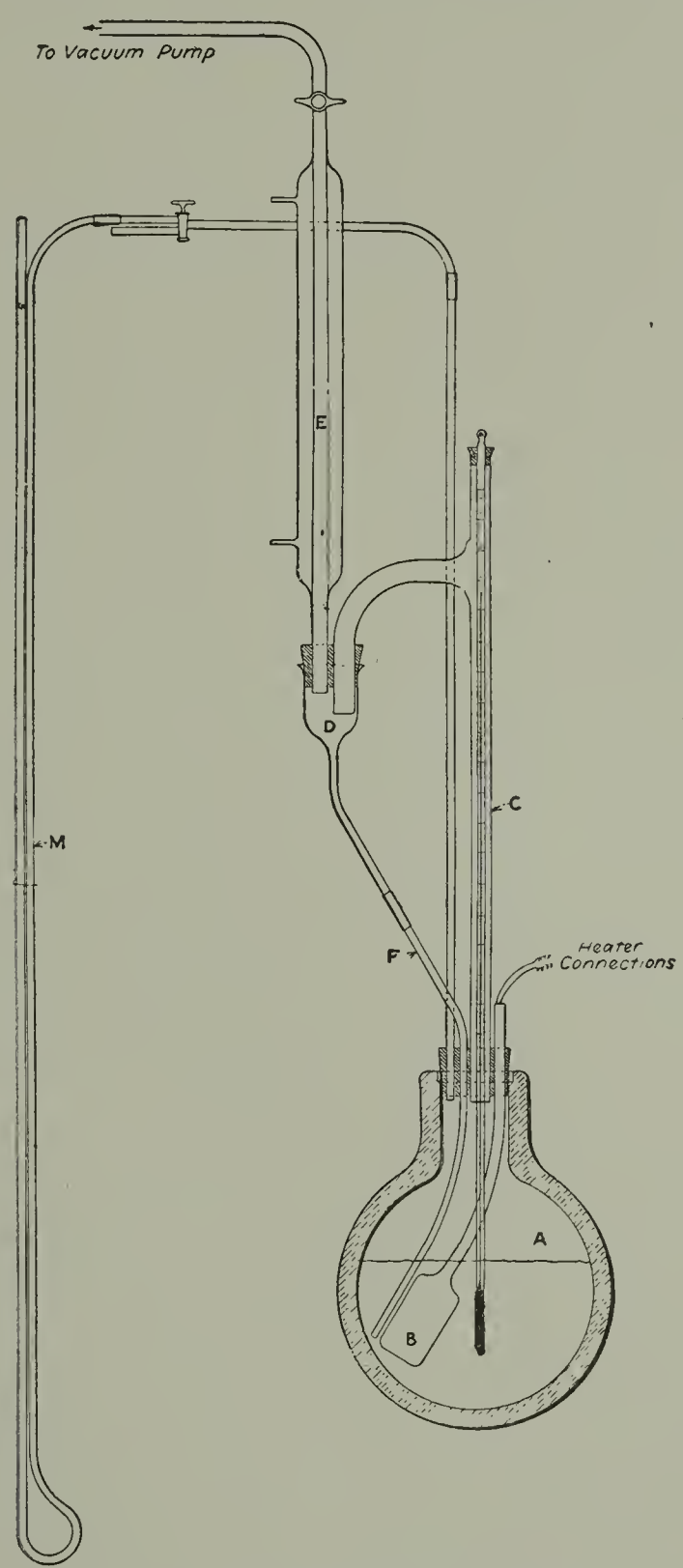
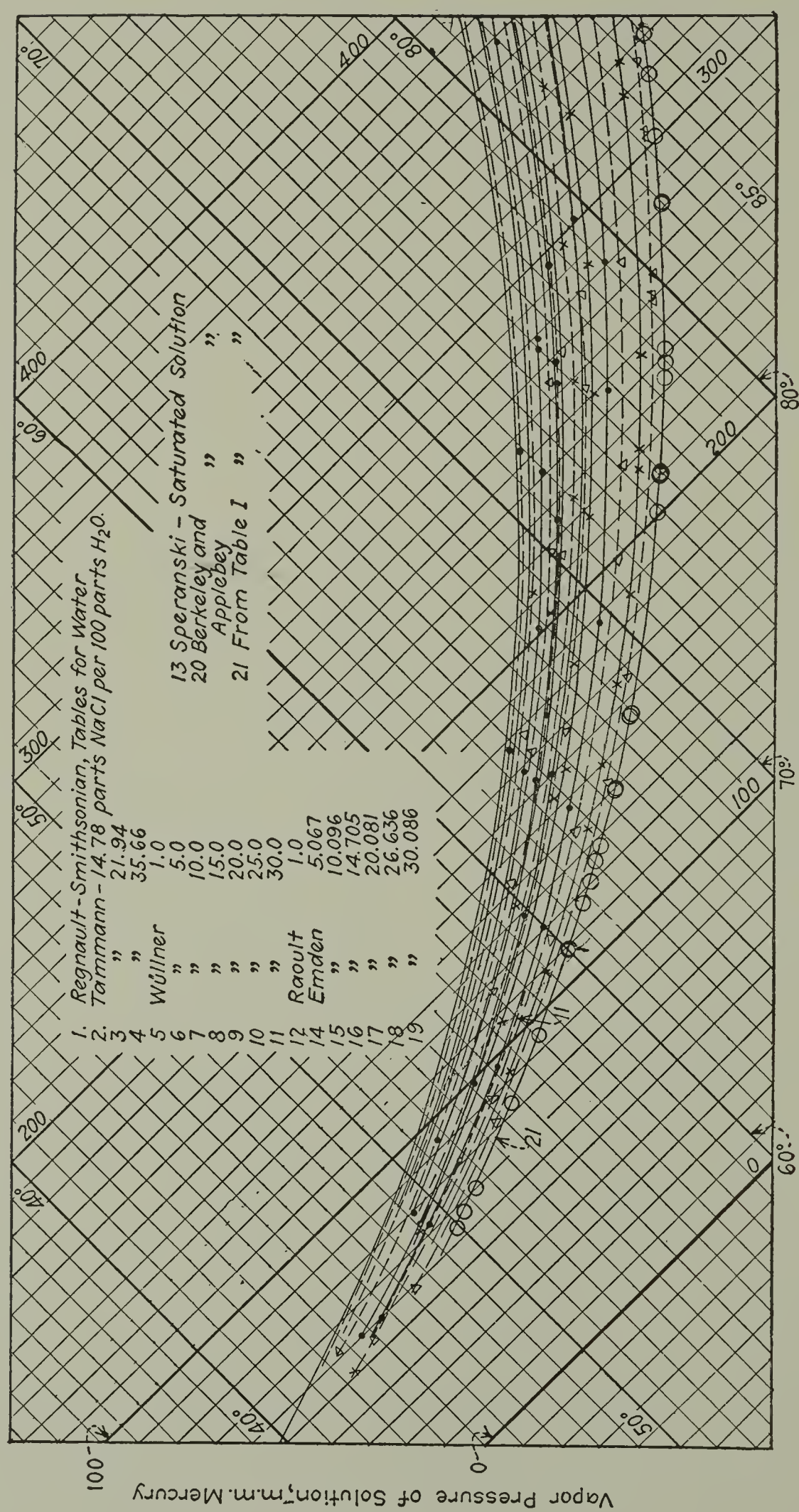


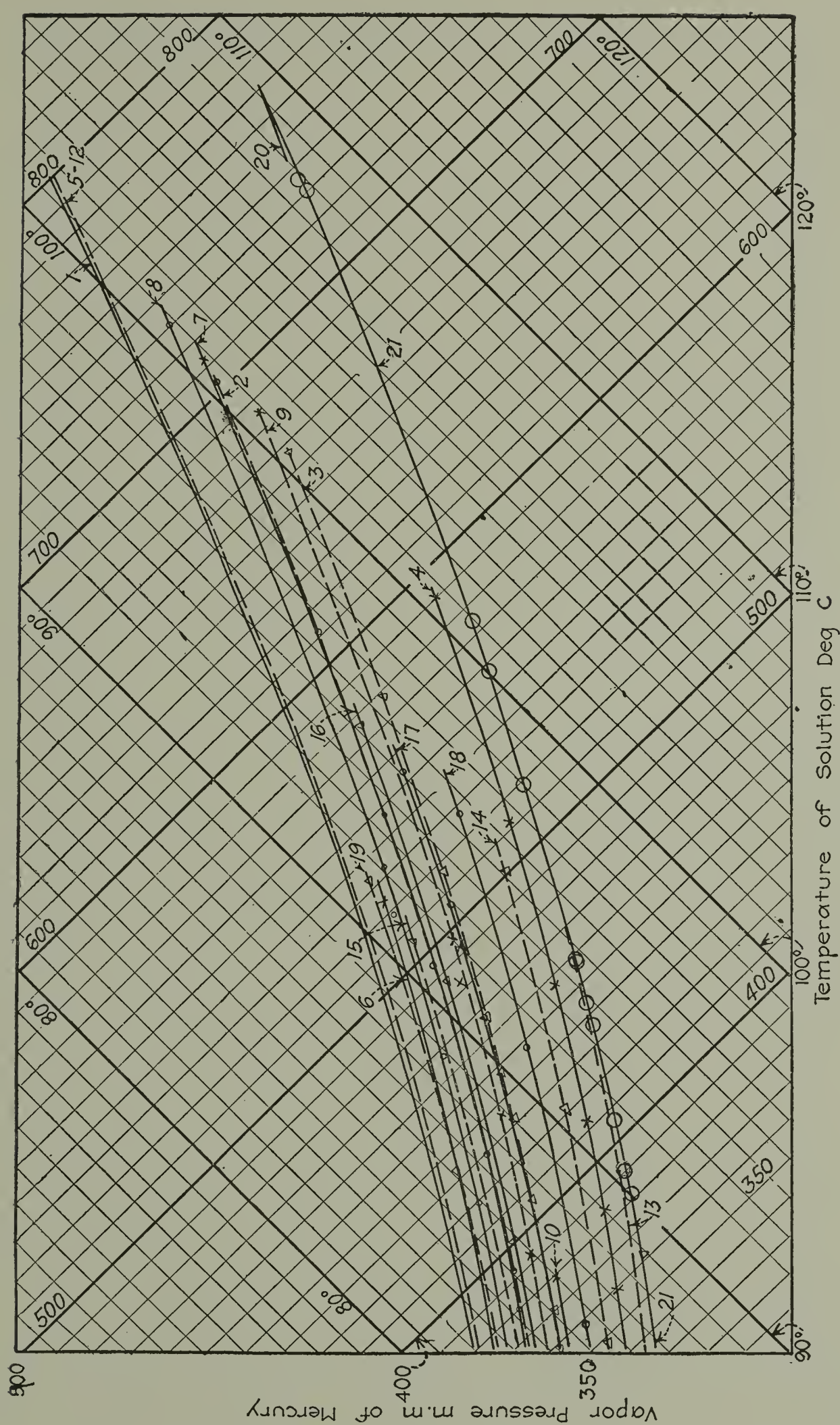
FIG. 1.—Boiling-point Apparatus.

Madison on the theory of osmose, not as yet published,[1] shows that such relations can not be expected to hold rigidly in the case of electrolytes. It therefore seems unprofitable to go into a theoretical

[1] By personal communication.



CURVE I.—Vapor Pressure of NaCl Solutions at Various Temperatures.



CURVE I. (*Continued*)

discussion of these factors in this paper, but a bibliography of articles dealing with this question and methods of determining boiling points is appended.

The direct determination of the vapor pressure of the solution under the desired conditions of temperature and pressure either by the static or ebullistic methods is far more satisfactory than an attempt to get at it from theoretical considerations or empirical formulations.

The work on sodium chloride was therefore divided into two parts: first, a determination of the boiling point of saturated sodium chloride solution over the temperature range 50° C. to the boiling point at 760 mm. pressure, to supplement the values found in the literature, and second, a critical study of the values given for the boiling points (or vapor pressures) of salt solutions of various concentrations over the range of temperatures and pressures employed in evaporator practice.

Several types of boiling point apparatus were experimented with, but the apparatus finally used is shown in the accompanying cut, Fig. 1. The drawing is nearly self explanatory. A saturated solution of sodium chloride, together with an excess of salt was placed in the 2-liter flask *A*, which was protected from radiation and air currents by a layer of asbestos $\frac{1}{2}$ inch thick, molded onto the flask. The solution was heated by the small electric heater *B*. The amount of heat input, or rate of boiling was regulated by varying the current by means of an external resistance in series with the heater. The vapor passed up around the thermometer through the tube *C*, which was also protected with asbestos covering, except at the point where temperatures were being read, thence to the trap *D*, and the condenser *E*. All condensed water was returned to the flask at the base of the heater by the tube *F*. By thus steam jacketing the thermometer, the steam correction to the reading taken was reduced to 0.12° C. for the maximum correction for the temperature of the emergent stem. The vacuum was measured by the U manometer *M* which communicated directly with the flask, thus measuring the pressure at a point very near the thermometer bulb. The importance of this precaution is well shown by E. von Rechenburg.[1] The vacuum was maintained and regulated by means of an ordinary laboratory water jet vacuum pump. In this way, it was possible to hold the vacuum steady within 1 to 2 mm. for periods

[1] J. Prakt. Chem., 79, 475.

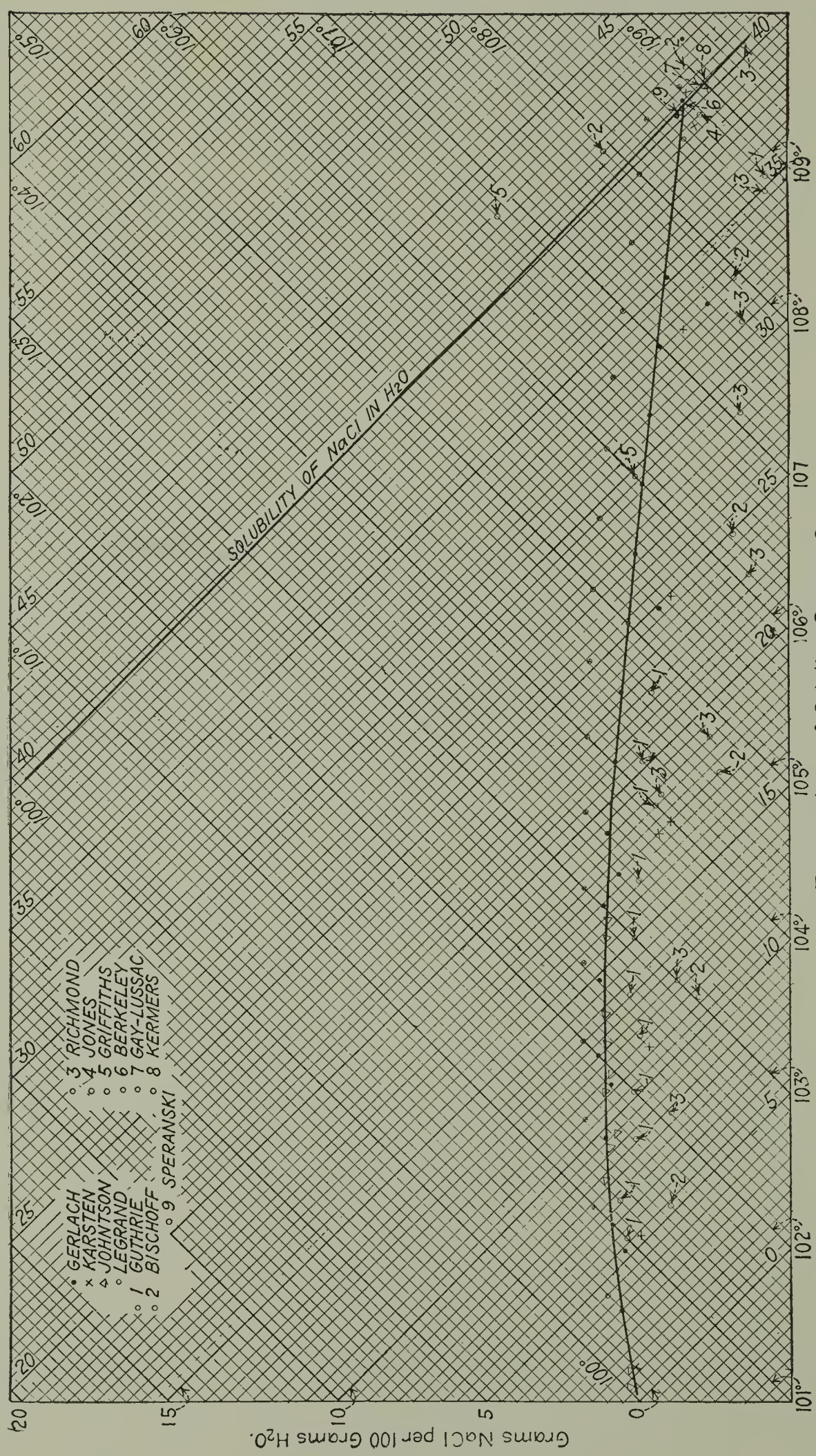
of over 30 minutes, during which a number of simultaneous readings of vacuum and temperature could be taken. The vacuum readings were corrected for the temperature of the mercury, before subtracting from the barometer to give the absolute pressure. The thermometer used for the readings below 100° C. was graduated in tenths of degrees, and the thermometer used for the higher temperatures was graduated in fifths of a degree. These were both certified thermometers, which had been rechecked at the boiling point of water. It should be remembered that the values were wanted for engineering design, and that an accuracy of 0.1° C. or 2 mm. of mercury would be amply accurate for this purpose.[1] The values so obtained are given in Table I. This table also includes some values obtained with essentially the same apparatus, but with different methods of heating. In one case the heating was done by a small copper coil placed in the solution and heated by means of steam, and in the other case direct heating by a gas flame was used.

The study of the values given in the "Standard" tables and scattered through the literature was carried out as follows: The data could be separated for the most part into two divisions, (*a*) the vapor pressure of certain NaCl solutions over a range of temperatures, and (*b*) the boiling point of various NaCl solutions at 760 mm. pressure. Curves I and II were then plotted on a very large scale. Curve I showed the values given for the vapor pressure of NaCl solutions over a range of pressures. Values below 50° C. were discarded as not being pertinent. Smooth curves were drawn through the points given by each investigator. Our results for saturated sodium chloride solutions were included in this graph. From curve I a table was made up showing for each 5° interval, from 50° C. to 100° C., the concentration of sodium chloride and the corresponding vapor pressure given by each investigator.

Curve II showed various concentrations of NaCl solutions plotted against their boiling points under 760 mm. pressure. Some of the points at the same concentration differ by over 2° C.[2] At this point it was found necessary to know the solubility of NaCl at different temperatures. For this purpose curve III was plotted showing grams

[1] Many values given in the literature were found to differ by two full degrees C. even though pressures were expressed in hundredths of millimeters, and temperatures in thousandths of a degree.

[2] The values given by Droop Richmond, Gmelin-Kraut, 7th ed., vol III, p. 359, should be for per cent NaCl instead of g. NaCl per 100 g. H_2O.



CURVE II.—Boiling Point of NaCl Solutions at 760 mm. Pressure.

TABLE I

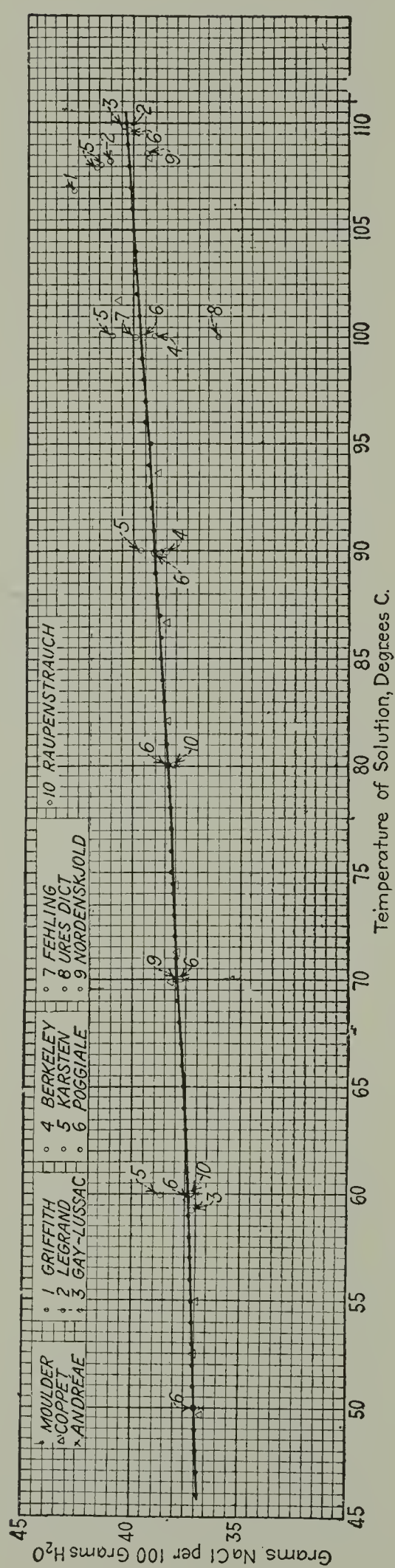
VAPOR PRESSURES OF SATURATED SALT SOLUTIONS

EXPERIMENTAL VALUES

Mean Values of Temp. of Solution C°.	Vapor Pressure mm. of Mercury.	Number of Readings Average to give Mean Values Cols. 1 and 2.	Mean Values of Temp. of Solution C°.	Vapor Pressure mm. of Mercury.	Number of Readings Averaged to give Mean Values, Cols. 1 and 2.
107.90	735.7	20	78.16	239.3	3†
107.80	731.6	40	77.87	236.7	4
108.84	575.0	2*	75.30	213.5	10
99.90	558.0	5*	75.23	212.1	10
97.92	518.7	3*	73.98	201.5	4*
94.68	456.9	10	68.11	155.3	7
94.66	458.0	10	68.04	154.0	7
93.83	444.9	4*	65.86	139.0	10
93.39	437.3	3*	65.70	138.3	10
91.37	406.0	3*	63.85	127.0	9
90.38	391.8	4†	63.36	123.9	7
90.02	381.5	10	62.73	120.2	5
89.98	381.0	10	61.82	116.7	10
86.36	331.6	10	60.27	109.6	5*
86.24	329.9	10	60.05	108.4	10
85.13	319.5	8†	57.38	92.9	20*
83.66	301.5	6*	54.79	84.2	4*
82.44	281.9	7	51.59	70.0	7
82.25	280.3	12	50.61	67.7	5
78.56	242.5	9	50.04	64.8	4*

* Heating by direct heat.
† Heating by steam coil.
Other values heating by electrical heater.

NaCl dissolved by 100 grams H_2O at various temperatures as given by different investigators. A smooth curve was drawn, and this curve was taken as giving the true solubility of NaCl in H_2O. Values read from this curve are given in Table II. These values were also plotted on Curve II, and a smooth curve was then drawn through the values previously plotted, and extending just up to this solubility line. In drawing curves II, III, and IV an effort was made to weight the values according to the care, accuracy and date of the original investigations.



CURVE III.—Solubility of Sodium Chloride.

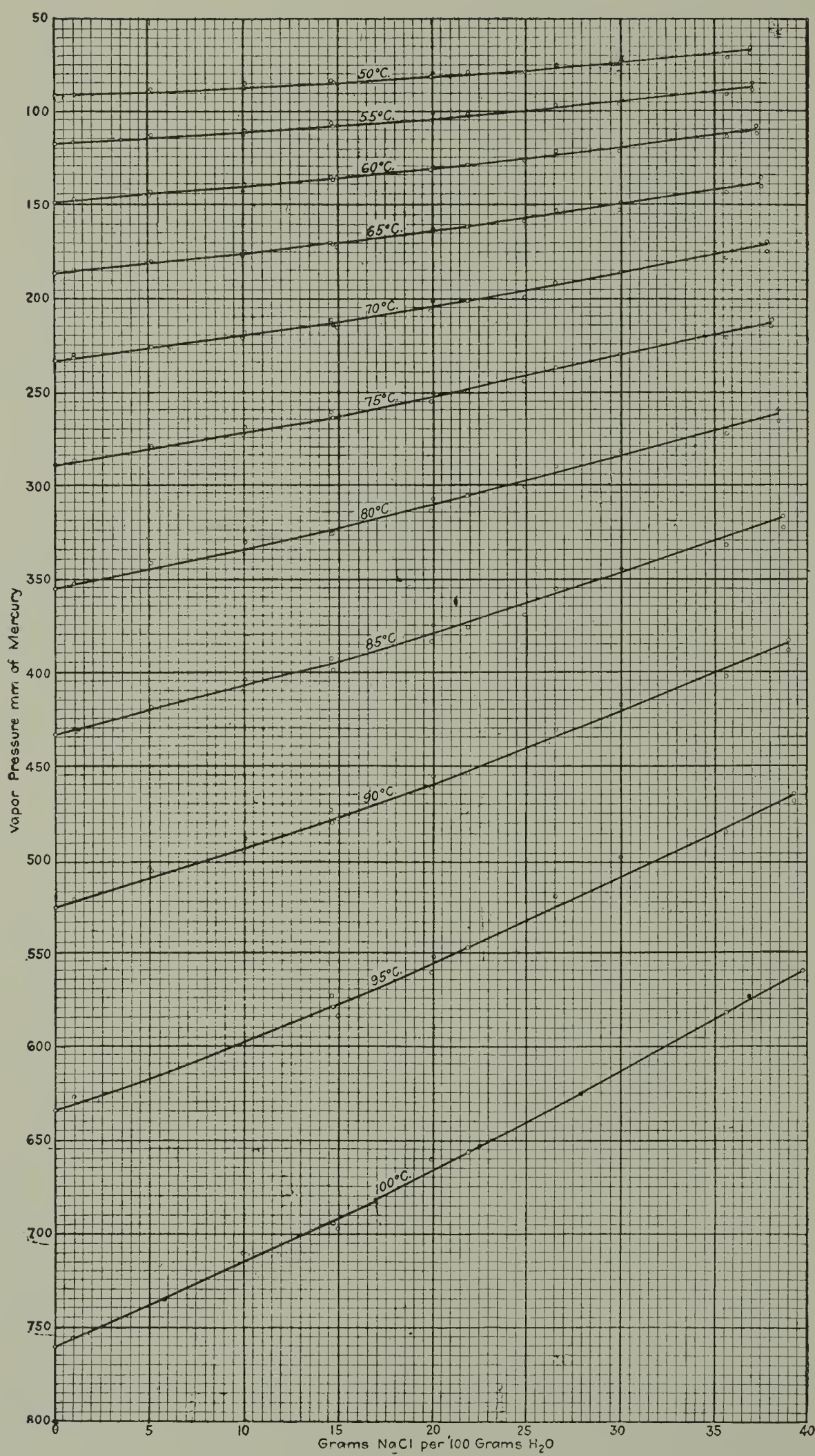
TABLE II

SOLUBILITY OF NaCl IN H_2O

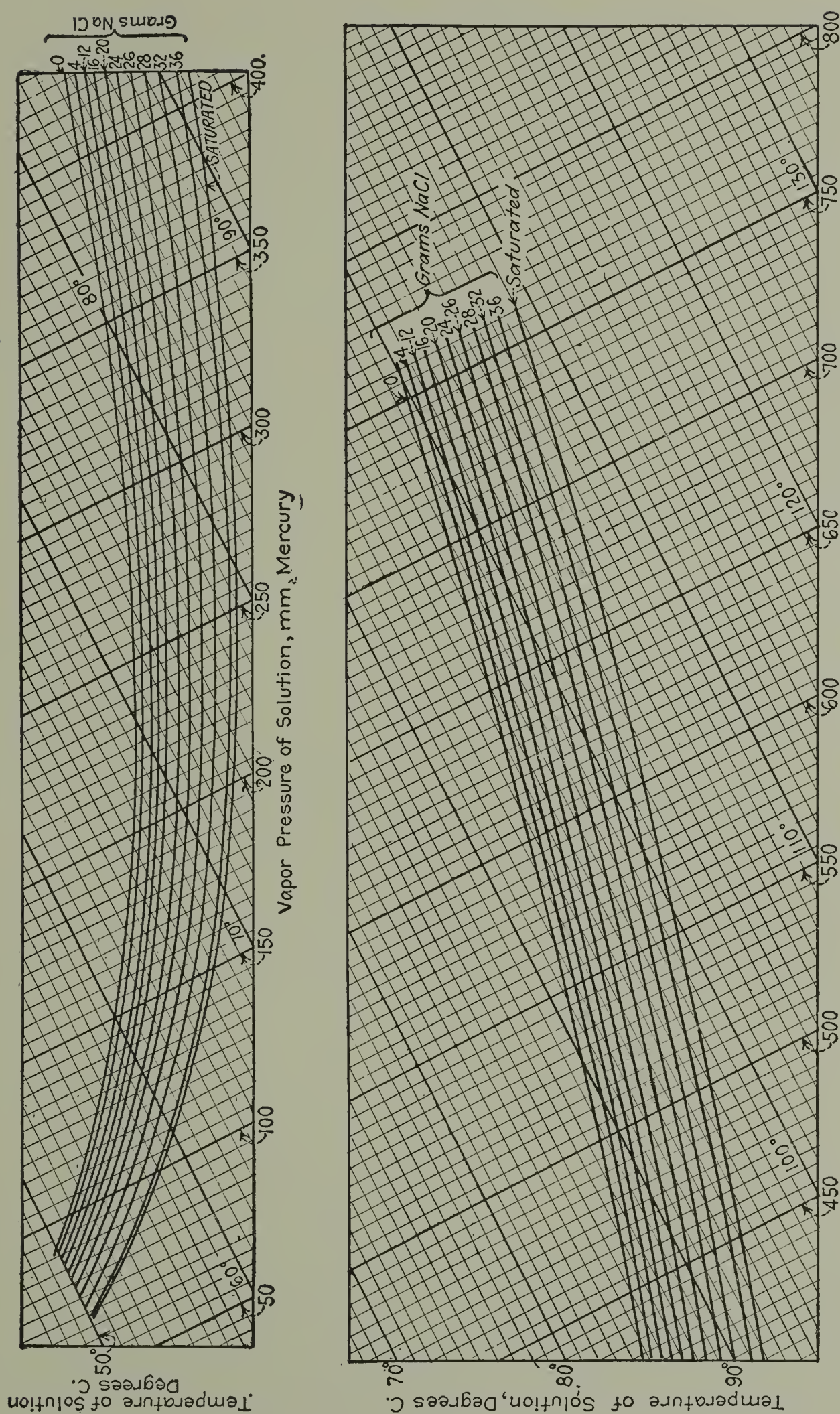
Values read from Curve III

Temperature ° C.	Grams NaCl Dissolved by 100 grams H_2O at Temp. T.	Temperature° C.	Grams NaCl Dissolved by 100 grams H_2O at Temp. T.
50°	36.95	101°	39.80
55°	37.05	102°	39.88
60°	37.30	103°	39.93
65°	37.55	104°	40.00
70°	37.85	105°	40.08
75°	38.12	106°	40.15
80°	38.40	107°	40.23
85°	38.70	108°	40.30
90°	39.00	109°	40.37
95°	39.30	110°	40.45
100°	39.70		

Curve IV was next plotted from data obtained from curves I and III. That is, for each 5° interval, from 50° to 100° C., the vapor pressures of solutions of concentrations ranging from pure water to saturated solution were plotted against the corresponding concentrations. The concentration for the saturated solutions was taken from curve III. The 100° C. curve was supplemented by values given by Tammann for the vapor pressure of salt solutions at 10° C., these data being plotted as solid circles. Smooth curves were drawn through these points, thus giving mean values for the vapor pressure of solutions of various concentrations at 5° temperature intervals. Table III, showing the vapor pressure at these temperatures of solutions of various concentrations was then made up by reading values from curve IV. Table IV, derived from curve II, shows the temperature at which solutions of various concentrations have a vapor pressure of 760 mm. From these values curve V was plotted, which shows the vapor pressure at different temperatures of water, of solutions containing 4, 8, 12, 16, 20, 24, 28, 32, and 36 grams NaCl per 100 grams H_2O, and of saturated NaCl solution. It is noteworthy that smooth lines, conforming in curvature with the curve for pure water, could be drawn through *every* point so plotted. From this it is inferred that there could be no great error in the values given by either curves II or V.



CURVE IV.—Vapor Pressure of Sodium Chloride Solutions at Certain Temperatures.



CURVE V.—Vapor Pressure at Various Temperatures of Various NaCl Solutions.

Curve V is useful in giving a close approximation of the temperature drop available for heat transference in a salt pan. The temperature of the vapor coming from the solution in any effect is the temperature at which water would boil under the pressure P_1, existing in that body, and hence may be read from the curve, $G=0$ (call this temperature t_1). Now if the mean hydrostatic head

TABLE III

VAPOR PRESSURES OF SODIUM CHLORIDE SOLUTIONS

Values read from Curves

	Grams NaCl per 100 gm. H_2O.	Vapor Pressure of Solution at Temperature of										
		50°C.	55°	60°	65°	70°	75°	80°	85°	90°	95°	100°
	0	92.0	117.5	148.8	186.9	233.1	288.5	354.6	433.0	525.4	633.8	760
	4	90	115	145	183	228	282	347	423	513	620	743
	8	88	113	141	178	220	275	38 ε	412	500	605	725
	12	86	110	138	174	217	268	329	401	487	589	769
	16	84	107	134	169	211	261	320	390	474	573	687
	20	81	103	130	163	204	252	310	379	460	555	666
	24	78	100	126	158	797	244	300	366	444	537	646
	28	75	96	121	152	190	234	289	353	428	519	624
	32	71	92	116	146	182	226	278	339	412	500	602
	36	67	87	110	139	174	216	267	325	395	481	580
Saturated solutions	Grams NaCl per 100 gm. H_2O	36.95	37.05	37.30	37.55	37.85	38.12	38.40	38.70	39.00	39.30	39.70
	Vapor Pressure	66	86	108	137	170	212	261	316	383	465	559

expressed in mm. of mercury, is added to P_1, the mean total pressure in the boiling liquid, P_2, is obtained. On curve V follow over the pressure P_2 until the particular concentration of salt existing in the pan is reached. The abscissa corresponding to this point gives the mean temperature, t_2, at which the solution boils. The difference between these two temperatures, t_2-t_1, is temperature drop lost due to excess boiling point and hydrostatic head. The difference

TABLE IV

TEMPERATURE AT WHICH NaCl SOLUTIONS HAVE A VAPOR PRESSURE OF 760 MM.

(Values read from Curve II)

Grams NaCl per 100 grams H_2O.	Temperature of Solution ° C.	Grams NaCl per 100 grams H_2O.	Temperature of Solution ° C.
0	100	24	104.6
4	100.6	28	105.6
8	101.2	32	106.6
12	102.0	36	107.6
16	102.8	40.37 (Sat.)	108.7
20	103.7		

between the temperature of the vapor coming from the previous effect and t_2 is the temperature drop really available to cause transference of heat through the heating surface.

A complete table of values was read from curve V, this data being given as Table V. This table gives the temperature at which the various solutions have a certain vapor pressure, as the data is most serviceable for evaporator design in this form. A "straight line" interpolation may be used between adjacent values to obtain intermediate values without increasing the error of the results. The plotting was carried out carefully,[1] and to large scale, and it is felt that the values given in Table V are reliable to within certainly 0.2° C. and 3 mm. pressure. All of the erratic results given in the regularly accepted standard tables have been eliminated, and the field from 50° C. to the temperature at which the solutions will boil under one atmosphere pressure is given in much greater detail than hitherto. The values for saturated sodium chloride under diminished pressure are not found in any of the regular published tables. The results given are dependable to an accuracy which is more than sufficient for engineering design or industrial work. To obtain closer values, the original work would have to be repeated with apparatus of great refinement.

Determinations are now being made on caustic (NaOH) solutions of various concentrations, over a large range of pressures, after which the work will be repeated with the same solutions, saturated

[1] The use of heavy ink lines in preparing these curves for publication caused a loss of much of the original accuracy.

TABLE V

VAPOR PRESSURE OF SODIUM CHLORIDE SOLUTIONS AT VARIOUS TEMPERATURES

Values from Curves

Vapor Pressure of Solution at Temperature T.	Temperature of Solutions Containing G Grams N_2Cl per 100 Grams H_2O.										
	$G=0$	$G=4$	$G=8$	$G=12$	$G=16$	$G=20$	$G=24$	$G=28$	$G=32$	$G=36$	Saturated Solution.
760	100.0	100.6	101.2	102.0	102.8	103.7	104.6	105.6	106.6	107.6	108.7
740	99.3	99.9	100.5	101.3	102.1	103.0	103.9	104.9	105.8	106.8	108.0
700	97.8	98.4	99.0	99.8	100.6	101.5	102.4	103.4	104.3	105.3	106.5
660	96.1	96.8	97.4	98.2	98.9	99.8	100.7	101.8	102.7	103.7	104.8
620	94.4	95.0	95.7	96.5	97.2	98.0	99.0	99.9	100.8	101.9	103.0
580	92.6	93.3	93.9	94.6	95.4	96.2	97.1	98.0	99.0	100.0	101.1
540	90.7	91.4	92.0	93.7	93.5	94.2	95.2	96.1	97.1	98.1	99.0
500	88.7	89.4	90.0	90.7	91.4	92.1	93.1	94.1	95.0	96.0	96.7
460	86.5	87.3	87.9	88.5	89.2	90.0	90.9	91.9	92.9	93.9	94.7
420	84.2	84.8	85.5	86.2	86.9	87.6	88.5	89.5	90.5	91.6	92.3
380	81.7	82.3	83.0	83.6	84.3	85.1	86.0	86.9	87.9	89.0	89.8
340	78.9	79.6	80.2	80.8	81.5	82.3	83.2	84.1	85.1	86.1	86.9
320	77.5	78.1	78.7	79.3	80.0	80.8	81.7	82.6	83.5	84.6	85.3
300	75.9	76.5	77.1	77.7	78.4	79.2	80.0	80.9	81.9	82.9	83.6
280	74.3	74.9	75.5	76.1	76.7	77.5	78.3	79.2	80.2	81.2	81.8
260	72.5	73.1	73.7	74.2	74.9	75.8	76.6	77.4	78.4	79.4	79.9
240	70.7	71.2	71.8	72.4	73.0	73.8	74.6	75.5	76.4	77.5	77.9
220	68.7	69.2	69.8	70.3	70.9	71.7	72.5	73.5	74.3	75.4	75.9
200	66.5	67.0	67.6	68.1	68.8	69.6	70.4	71.2	72.2	73.1	73.7
180	64.1	64.7	65.3	65.8	66.4	67.2	67.9	68.8	69.8	70.8	71.2
160	61.6	62.1	62.7	63.2	63.8	64.6	65.3	66.1	67.1	68.1	68.6
140	58.6	59.2	59.8	60.3	60.8	61.5	62.2	63.1	64.1	65.2	65.6
120	55.4	55.8	56.3	56.9	57.5	58.1	58.9	59.8	60.7	61.8	62.2
110	53.6	54.0	54.5	55.1	55.7	56.2	57.0	57.9	58.8	60.0	60.3
100	51.7	52.0	52.5	53.0	53.6	54.3	55.0	55.9	56.8	57.9	58.2

with NaCl under the given conditions. This will place at our disposal for the first time, information on which the capacity of caustic evaporators working on cell liquors may be properly designed.

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BIBLIOGRAPHY

Determinations of the boiling-points of sodium chloride solutions, and theoretical discussions of the elevation of the boiling-points of solutions.

Andrea, J. prakt. Chem., **29**, 456.
Applebey and Hughes., J. Chem. Soc., London, **107**, 1798.
Baumé and Tsakalotos, Comp. rend., **144**, 373.
Beckmen, E., Z. Physik, Chem., **64**, 506, **79**, 177.
Berkeley, Trans. Roy. Soc., London, **203***A*, 206.
Berkeley and Applebey, Proc. Roy. Soc., London, **85***A*, 477.
Besson, A. A., Chem. Ztg., **37**, 1035.
Bischoff, Storer's Dict., Sol., p. 182.
Callendar, H. L., Proc. Roy. Soc., London, **80***A*, 466.
Carnelly, Melting and Boiling Point Tables, Vol. II.
Comey, Dict. of Chem. Solubilities.
Coppet, Ann. chim. phys., **30**, 411, 427.
Cottrell, F. G., J. Am. Chem. Soc., **41**, 721.
Edwards, A., J. Soc. Chem. Ind., **37**, 38T.
Emden, Wied. Ann., **31**, 162.
Fehling, Annalen der Pharmacie, **77**, 382.
Gay-Lussac., Ann. chim. phys., **11**, 310.
Gerlach, Z. anal. Chem., **26**, 438.
Gmelin-Kraut, Handbuch der anorg. Chem.
Griffiths, Q. J., Science, **18**, 90.
Guthrie, Phil. Mag., **4**, 6, 17, 49.
Johnston, Trans. Roy. Soc., Edinburgh, **45**, 193.
Jones, Chem. Soc., London, **33**, 182.
Kahlenberg, J. Phys. Chem., **5**, 339.
Karsten, Archiv., **20**, 45.
Kendall, J., J. Am. Chem. Soc., **36**, 1069.
Kiplinger, J. Am. Chem. Soc., **40**, 1020.
Landolt Börnstein, Physik. Tabellen.
Legrand, Ann. chim. phys., **2**, 59, 431.
Lovelace, Frazer and Miller, J. Am. Chem. Soc., **38**, 515.
Möller, Pogg. Ann., **117**, 386.
Mulder, Scheik. Verhandel (1864), 37.
Pauchon., Comp. rend., **89**, 753; **38**, 211.
Pavlivich, Z. physik Chem., **84**, 169.
Perman and Price, Trans. Faraday Soc., **8**, 68.
Poggiale, Ann. chim. phys., **8**, 469.

Porter, Proc. Roy. Soc., London, **79***A*, 521.
Ranson, Science, **43**, 686.
Raoult, Compt. rend., **87**, 167, and J. Chem. Soc., London, **36**, 4.
Raupenstrauch, Mon. Chem., **6**, 563.
von Rechenburg, E. J. prakt. Chem., **79**, 475.
Richmond, Analyst, **18**, 142.
Riesenfeld and Milchsack, Z. anorg. Chem., **85**, 401.
Rosanoff and Duphy, J. Am. Chem. Soc., **36**, 1411.
Sakurai, J. Chem. Soc., **61**, 495.
Seidel, Sol. of Inorg. and Org. Substances.
Sluiter, Verslag. Akad. Wetenschappen Amsterdam, **23**, 920.
Smits, Chem. Weekblad, **13**, 1296.
Speranski, A., Z. physik. Chem., **70**, 519; **78**, 86; **84**, 160; **85**, 623.
Tammann, Mem. de l'acad. Petersburg, **35**. 1887; Wied. Ann., **24**, 530; Annalen der Physik und Chemie, **24**, 537.
Tsakatos, Compt. rend., **144**, 1104.
Washburn and MacInnes, J. Am. Chem. Soc., **33**, 1686.
Washburn and Reed, J. Am. Chem. Soc., **41**, 729.
Watts' Dictionary of Solubilities.
Wüllner, Annalen der Physik und Chemie, **103**, 542.

EXPERIMENTS ON THE CORROSION OF IRON AND STEEL

By WILLIAM D. RICHARDSON

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THE views on rust set forth in this paper were first publicly expressed in an address before the Chicago Section, American Chemical Society, January 18, 1910, and subsequently before various societies. The experiments described cover the period from 1908 to 1919, inclusive.

The chemist who has followed the experimental work done on the corrosion of iron and steel during the past ten or fifteen years must have noticed the apparently contradictory nature of many of the experimental results and conclusions drawn from them and must have felt that the theory of corrosion lacked some essential factor or factors to make it even an approximately complete generalization. No chemist to-day can safely predict on the basis of theory what metal or metals will corrode most or least under a given set of conditions and even with the results of the very large number of experiments, which have been made by different investigators, before him, it would be difficult for him to recommend with certain assurance the best metal for a given service. Much has been claimed for old-fashioned wrought iron, for iron or mild steel containing a small amount of copper, for very pure iron produced by the open-hearth process, for special finishes and for special protective coatings, and still in any given set of circumstances wherein iron and steel are exposed to the weather or to conditions which favor corrosion, there is always a doubt as to which of several metals will have the longest life and how the corrosion or pitting will proceed. The common statement of the theory of corrosion based on Nernst's theory of electro-motive force[1] while entirely convincing in the abstract fails when subjected to test, to explain the experimental results obtained. However, the electrolytic theory undoubtedly includes all the fun-

[1] Whitney, J.A.C.S., 25, 1394.

damental facts, and if it fails to explain the course of corrosion in any given instance, this is probably because some essential facts have been overlooked or have not been sufficiently emphasized and correlated.

It is a matter of common knowledge that after the process of corrosion has once gotten well under way, it usually follows a more rapid course than in the beginning. It is also well known that corrosion starts with greater difficulty on a polished surface than on a smooth but somewhat rough surface. Various investigators however, have shown the profound influence of surface conditions, including mill scale and oxygen, on the commencement and progress of corrosion in iron and steel. The present paper points to the conclusion that surface conditions in many cases so far outweigh the influence of the composition of the metal that they are decisive in determining the course of corrosion and that they are in most instances of greater importance than the composition.

Some years ago it was thought that it might be possible to develop an accelerated corrosion test in sulphuric acid which would give indications of the comparative resistance to corrosion of various samples of iron and steel, at least in the same classes.[1] However, it was soon noticed that there were great differences in the results obtained by the accelerated corrosion test in sulphuric acid when compared with service tests on the same metal. For example, of two kinds of steel, one might dissolve in sulphuric acid of a given strength in approximately one-half the time required for the solution of the other, yet when exposed to moist air, corrosion would be found to proceed with approximately equal rapidity. Many other cases of lack of parallelism between the course of corrosion under the accelerated test and under service tests might be given. These can only be explained by differences in surface conditions, including those affecting the E. M. F. of the local electrolytic circuits and those influencing polarization and depolarization, when the composition of metal is the same in comparative tests.

The salt spray method of J. A. Capp [2] is useful for disclosing pinholes and uneven or thin protective coatings and this is the purpose for which it was designed. As an accelerated corrosion test it would yield results comparable only to service conditions involving the same corroding influences.

[1] Proc. A.S.T.M., 7, 1907.

[2] Proc. A. S. T. M. 14; Part 1, 475 (1914) 18; Part 1, 237 (1918).

The obvious difference between iron dissolving in acids and corroding in the presence of water and oxygen, is the cleanness of the surface in the former case, and the presence of rust in the latter case. The rust is adherent if alternate wetting and drying occur, and loose and flocculent, usually, if the iron is continuously wet or submerged.

Another difference, so obvious, between the two cases, is the polarizing effect of hydrogen in the first instance.

A clean iron surface is usually maintained when corrosion takes place under conditions of continuous submergence, and this is especially true when the medium is quiescent. This surface condition approaches most closely to that of iron dissolving in acids, although the presence of rust, even though in a flocculent condition, must be taken into account. The depolarizing effect of the moderate amount of oxygen present is also an active influence when the surface of the watery medium is exposed to air.

This remarkable difference in the behavior of different samples of iron to acids and in service tests requires explanation, since the solution of iron in acids and the ordinary corrosion of iron are such intimately related phenomena.

The ferroxyl indicator of Walker and Cushman is a most useful instrument for investigating corrosion phenomena, and can be usefully applied in the present investigations.

Walker has shown that a marked difference of potential exists between mill scale and bright iron.

Preliminary Experiments—Series I.

If a piece of piano wire (99.85 per cent iron) or pure open-hearth iron (99.95 per cent iron) be carefully cleaned and rubbed with fine emery, bent U shape and one arm burned in a flame to coat this arm with magnetic oxide (the other arm remaining bright) and if the whole be submerged in ferroxyl jelly, the bright arm becomes quickly surrounded by a blue zone, showing an anodic region, and the oxidized arm by a red zone, showing a cathodic region. The cathodic character of mill scale can be shown also by its behavior toward diluted copper sulphate solution. After coating a piano wire with mill scale (in the flame) cross scratches are made, say $\frac{1}{16}$ to $\frac{1}{32}$ inch apart, exposing the bright iron beneath. When such a wire is inserted in dilute copper sulphate solution the copper begins to deposit on the magnetic oxide instead of on the exposed iron.

If a sheet of iron be allowed to corrode so that part of the mill

scale is removed, or if acid be applied in such a way as to uncover bright iron in spots and leave the scale intact in other places (producing a mottled effect) and if the sheet be then washed and dried, when the ferroxyl indicator is applied the blue and red regions correspond most precisely to the bright iron and mill scale areas respectively. A few exceptions to this general rule may occur owing to the mill scale covering being not quite perfect on the one hand and to the presence of invisible oxidized areas which have formed on the bright iron, during washing. Further, the red phenolphthalein pigment sometimes diffuses over the bright iron and the Turnbull's blue, not being diffusible, does not cover the bright iron until later.

If a strip of nearly pure iron be allowed to rust by contact with most filter paper or cloth, preferably in a closed chamber, and dried. and if one-half be cleaned to expose bright iron; and if the strip be then bent to U shape and submerged in ferroxyl jelly, the clean part becomes anodic, the rusty arm cathodic. Small regions of the rusted arm may become anodic owing to the fact that the rust has not adhered closely enough to cover entirely the bright iron but by far the greater part if not all will in all experiments be cathodic.

The last experiment may be performed in another way. A piece of nearly pure iron is pickled to remove mill scale, washed and dried. Drops of water are then sprinkled over the surface and allowed to dry in the air at a low temperature, whereupon spots of the rust are produced conforming closely to the original configuration of water drops. After the ferroxol jelly is poured over the surface the blue and red areas correspond precisely with the areas of bright iron and rust respectively. The rust spot areas always become cathodes, usually entirely, always in part. The bright spots become anodes for the greater part although it is true that occasionally a red area develops over apparently bright iron. But it is possible that in these exceptional cases the apparently bright iron is covered by a thin invisible oxidized layer. In experiments of this sort the outer edge of the jelly where it is in contact with the metal always turns bright red. This point will be briefly discussed.

It is interesting to note the effect of pouring the ferroxyl jelly on cleaned bright "pure" open-hearth iron. A red border forms at the outer edge of the jelly almost immediately, showing that the metal here is cathodic. Next to this a blue band develops and the interior is at first faint pink, but in the end the interior usually becomes blue provided the ferroxyl jelly covers only a moderate area.

The red border, which is always intense, begins to form at the extreme outer edge of the jelly where it is in contact with the metal. Here the oxygen of the air would have the greatest depolarizing action and it is reasonable to suppose that we have here in effect the action of an oxygen cathode. In connection with the rust and mill scale experiments, this one is interesting in showing how surface conditions may easily outweigh in electrolytic effect the varying compositions of iron and steel. The rusting experiments with ferroxyl jelly may be repeated with any kind of ordinary sheet iron (including mild steel) with the same results. No kind of iron or steel has been found which did not react in the same way.

Earlier Tests. Series 2 Experiments

Some years ago when enterprising American manufacturers put on the market a very pure iron made by the open-hearth process the product was hailed with joy by users of iron, who were led to believe on the basis of the electrolytic theory of corrosion that this new and pure form of iron would resist corrosion better than the common varieties. The iron in question contained (by difference) from 99.94 per cent to 99.95 per cent pure iron, as a rule. All the investigators who did pioneer work on the electrolytic theory of corrosion, particularly in the United States, were unanimous in believing that a pure iron of this type ought to show great corrosion-resisting qualities. These points are now matters of history and in brief it may be stated that the new iron did not come up to expectations as regards corrosion-resisting qualities. When this iron was first introduced considerable quantities of it, both plain and galvanized, were bought and put to various uses, but it was not found in practice that the iron had any advantage as regards corrosion-resisting qualities over ordinary open-hearth sheet iron or mild steel. Therefore an investigation of its qualities was begun beginning with acid tests. The iron dissolved very slowly in 5 per cent sulphuric acid and in fact so resisted the action of the acid that it was thought it should possess great corrosion-resisting qualities in service. Many samples were tested in acid against wrought iron, ordinary open-hearth iron, Bessemer iron and cast iron and in all cases similar results were obtained. The new iron dissolved much more slowly than the others. In spite of these acid tests there was a reasonable doubt as to the corrosion-resisting qualities of the iron under atmospheric conditions

in service. Practical tests, under identical circumstances, of the new iron in comparison with common open-hearth sheets were not proving the new metal to have better corrosion-resisting qualities than the old. Consequently other tests were demanded. A series of tests known as Series 2 Experiments was begun as follows:

Twelve pieces of common sheet iron or mild steel and twelve pieces of the pure open-hearth iron were suspended alongside of each other in distilled water at rest and in 10 per cent sodium chloride brine at test, in distilled water with air agitation and in 10 per cent sodium chloride brine with air agitation. The pieces were of definite area and were all weighed when put into the various liquids. They were taken out at intervals, the adhering rust removed by suitable means, weighed and the loss in weight calculated to grams per square centimeter. It was thought that conditions represented several service conditions as well as could be expected, having advantages over several other methods which suggested themselves; for practical reasons also, the surface of the pieces was not changed by the removal of mill scale before immersion, inasmuch as it was thought best to test the iron as received from the mill. The layer of mill scale on the surface of the metal afforded some protection for a time, but the corrosion gradually removed it, so that ultimately all the pieces were bright under the rust. This removal of the magnetic oxide layer occurred sooner in some pieces than in others, but working on averages there was no essential difference, at various stages, in the pieces of new iron as contrasted with the common iron.

Analyses of the two kinds of iron (or mild open-hearth steel) used in these experiments are shown below:

	Open-hearth Pure Iron.	Common Iron.
Silicon	.004	.028
Phosphorus	.002	.021
Sulphur	.014	.063
Manganese	.021	.457
Total Carbon	.025	.253
Copper	.020	.025

In brief, the results of these experiments showed that the new iron had no advantage whatsoever over ordinary open-hearth sheet iron as regards rust-resisting qualities.

The loss in grams per square centimeter was practically identical, on the average, in each case. After eighty-four days' immersion the results were as follows (Table I):

TABLE I

SERIES 2 EXPERIMENTS

	Water at Rest. Loss per sq. cm. in Grams.	10% Brine at Rest. Loss per Sq. Cm. in Grams.	Water with Air Agitation. Loss per Sq. Cm. in Grams.	10% Brine with Air Agitation. Loss per Sq. cm. in Grams.
Pure Open-hearth Iron	0.0098	0.0079	0.0485	0.0353
Pure Open-hearth Iron	0.0152	0.0085	0.0405	0.0381
Pure Open-hearth Iron	0.0146	0.0082	0.0410	0.0392
Pure Open-hearth Iron	0.0164	0.0074	0.0377	0.0525
Pure Open-hearth Iron	0.0132	0.0094	0.0416	0.0371
Pure Open-hearth Iron	0.0130	0.0069	0.0377	0.0372
Average	0.0137	0.0080	0.0411	0.0399
Common Open-hearth Iron	0.0103	0.0074	0.0455	0.0361
Common Open-hearth Iron	0.0132	0.0060	0.0357	0.0393
Common Open-hearth Iron	0.0134	0.0077	0.0421	0.0457
Common Open-hearth Iron	0.0086	0.0072	0.0379	0.0395
Common Open-hearth Iron	0.0122	0.0071	0.0408	0.0398
Common Open-hearth Iron	0.0152	0.0069	0.0400	0.0412
Average	0.0121	0.0070	0.0403	0.0402

The conclusions drawn from these experiments and from other practical tests was that iron of the purity attained, namely, 99.95 per cent, had no advantage in rust-resisting qualities over ordinary iron or mild steel, whatever gain there might be in physical properties.

SERIES 3 EXPERIMENTS

This series of experiments was started in order to ascertain how much acceleration of corrosion could be brought about by pure oxygen over that induced by air alone. The plates used in the experiments were ordinary open-hearth black iron (mild steel) No. 16,

6×6 inches square. The conditions to which the plates were subjected were as follows:

1. Water with air agitation, two hours each day.
2. Water with air agitation for two hours each day, plates dried in the air on alternate days, three times per week.
3. Water with oxygen agitation, two hours each day.
4. Water with oxygen agitation, two hours each day, dried in the air on alternate days, three days per week.

The reason for limiting the agitation to two hours per day was the large amount of oxygen required if oxygen was used continuously. In conditions 3 and 4 an oxygen atmosphere was maintained (except when the plates were being dried) by confining the entire apparatus under a large bell jar. The results are shown in Table II.

The experiments were continued for 1000 days, but the conditions were such that the results are only comparable among themselves and cannot be compared with the results obtained in Series 4 Experiments. The results are interesting as indicating the importance of oxygen as an accelerator of corrosion. The plates which were hung submerged in water throughout the experiments, the water being kept saturated or nearly saturated with oxygen, lost 118 grams on the average in 1000 days, whereas the comparative experiment in which air was used produced a loss of 85 grams. Where the plates were exposed to air agitation and dried in air, there was a loss of 93.7 grams before the surfaces were cleaned and from the comparative plates where oxygen was used for agitation and which were dried in the air also, a loss of only 84.9 was recorded. After cleaning off the rust and scale by means of the sand blast, the former plates showed a loss of 167 grams and the latter of 139. The submerged plates remained clean throughout the experiment after the mill scale was removed and exhibited to the last a fairly smooth, finely crystalline surface which was covered during the progress of the experiment more or less with soft and flocculent ferric hydroxide. The results indicate clearly that pure oxygen is a more powerful corroding agent than atmospheric air, although corrosion in the presence of air is assisted by a small quantity of CO_2 which has been shown to work in a cyclic manner.[1] The plates which were dried in the air and hence subjected to the enormously accelerating effect of adherent rust were badly corroded and pitted. The oxygen plates were more severely pitted

[1] J. Newton Friend, The Corrosion of Iron and Steel, London, 1911, pp. 35 and 36 Whitney, J. A. C. S., 25, 394 (1903).

than the air plates. Nevertheless, the loss from the plates exposed to oxygen was less than from those exposed to air. This can be accounted for by the fact that the rust adhered more closely to the oxygen plates than to the air plates and while the deposit was not sufficiently uniform or extensive to protect the plates completely, nevertheless it served to reduce the loss even in the presence of oxygen which ordinarily, and without the protective action of the adherent rust, would have acted as a stronger corroding agent than the air. In this case the corroding agent and not the composition of the metal modified the behavior of the products of corrosion.

TABLE II.—SERIES 3 EXPERIMENTS.

COMPARISON OF AIR AND OXYGEN AS AGENTS OF CORROSION.

Age in Days.	Water, Air, Agitation.	Loss in Grams.		Water, Oxygen, Agtation, Dried.
		Water, Air, Agitation, Dried.	Water, Oxygen, Agitation.	
100	8.2	5.3	12.4	6.8
200	15.6	10.1	24.4	15.7
300	22.3	17.0	35.2	24.7
400	32.2	30.4	43.4	33.5
500	40.3	45.0	66.9	48.9
600	50.2	56.8	74.8	57.9
800	68.8	76.7	107.2	70.6
1000A	85.0	93.7	118.0	84.9
1000B	.....	167.0	.....	139.0

1000A represents loss before plates were cleaned.
1000B after removal of rust by the sand blast.

POTENTIAL DIFFERENCE. SOLUTION PRESSURE

Corrosion depends in part on the solution pressure of iron and its place in the electro-chemical series. While varying somewhat with the nature of the electrolyte used, this series as commonly given is as follows, beginning with oxygen at the negative end and ending with caesium at the positive end of the series. Hydrogen is placed differently in different tables, in some being shown as more, in others less electropositive than iron.

ELECTRO-CHEMICAL SERIES OF THE ELEMENTS

Non-metals.	Metals.		
—	Osmium	Hydrogen	Magnesium
Fluorine	Rhodium	Lead	Calcium
Oxygen	Iridium	Tin	Strontium
Chlorine	Gold	Nickel	Barium
Bromine	Platinum	Cobalt	Lithium
Iodine	Palladium	Iron	Sodium
Sulphur	Silver	Cadmium	Potassium
Phosphorus	Mercury	Zinc	Rubidium
Selenium	Copper	Manganese	Caesium
Nitrogen	Arsenic	Chromium	+
Boron	Bismuth	Aluminium	
Carbon	Antimony		
Silicon			

In this series the oxides of the metals are not placed, but it is well known that iron is strongly electro-positive to Fe_2O_3 and Fe_3O_4 as well as to oxygen itself. In the next table hydrogen is placed electro-positive to iron as well as electro-negative. The very lack of agreement on the exact position of a given element in the electro-chemical series indicates the influence of lesser factors in locating the element in one position or another. These factors are in general similar to those which influence and modify the course of corrosion.

In order to ascertain the place of hydrogen in relationship to iron in the electro-chemical series, the following experiment was tried, based on the well-known fact that a pure or nearly pure iron when soaked in dilute sulphuric acid absorbs considerable quantities of hydrogen.

Two strips of pure open-hearth iron, measuring about 1 inch by 3, were carefully cleaned by means of fine emery paper. One was allowed to soak in sulphuric acid of something less than 1 per cent strength overnight. In the morning the untouched piece of metal still bright, was once more repolished with fine emery and both pieces were connected through a sensitive milli-volt meter and simultaneously plunged into neutral salt solution. The volt meter showed the acid soaked iron positive and the clean iron negative.

On the face of it this experiment indicates that hydrogen, or rather iron with hydrogen occluded, is electro-positive to clean iron,[1]

[1] See Richards and Behr, "The Electromotive Force of Iron under Varying Conditions and the Effect of Occluded Hydrogen." Carnegie Instutution of Washington, 1906.

but it was considered that the experiment might only prove that completely reduced iron (iron with hydrogen occluded) was electro-positive to iron with oxygen condensed on its surface (clean bright iron). However, the conditions of the experiment were similar to those which might obtain during corrosion, so that it may be accepted for practical purposes that iron with hydrogen occluded on its surface or any area of iron with hydrogen occluded is electro-positive to clean, bright iron and, of course, more so to iron with occluded oxygen or coated with oxides or iron. This holds true for water, neutral salts and generally for dilute non-oxidizing acids.

Carbon (graphite) is electro-negative to iron and electro-positive to the oxides of iron and to oxygen.

The following table indicates the electro-chemical position of iron and the other substances concerned in corrosion phenomena together with a few other metals for comparison:

+
Aluminium
Zinc
[1] Hydrogen
Hydrogen occluded by iron
Iron
[1] Hydrogen
Copper
Iron Carbides
Gold
Carbon
Iron Oxides
Oxygen
—

It is not claimed that the order shown in this table is absolutely correct, but for the consideration of corrosion phenomena it is practically so and serves to visualize the position of the various elements concerned.

Factors Influencing Corrosion

The factors influencing corrosion considered in this paper are four in number:

1. Composition of the metal.

[1] Placed before iron by some authorities.

2. Physical treatment to which the metal has been subjected.
3. The influence of atmospheric oxygen (and other atmoshpheric constituents).
4. The influence of the products of corrosion or rust.

(1) Composition

According to the electrolytic theory, based on the solution pressure hypothesis of Nernst, corrosion of iron has been held by many chemists to be determined by the composition of the metal and perhaps the majority of papers written on the subject take this point of view. All of the kinds of iron and steel considered in this paper corrode easily with the single exception of Durion, which does not corrode at all. This metal is stated to contain approximately 15 per cent of silicon and hence is an alloy of so different a composition from the other metals considered as to require entirely separate treatment. It is possible that there are no or few ferrite areas or surfaces exposed in this alloy and hence little opportunity for iron, owing to its solution pressure, to go into solution under any conditions even in the presence of strong and weak acids. An investigation is needed of an entire series of iron-silicon alloys containing increasing percentages of silicon up to the quantity necessary to prevent corrosion and such a study should include crystallographic examination and corrosion tests. An investigation is also much needed of other iron alloys, including iron-nickel alloys and tool steels, from the standpoint of corrosion. There must be some point, more or less critical, at which corrosion or corrodibility rapidly diminishes or ceases and the study of the composition corresponding to this point or curve region should throw much light on the general problem of corrosion. For present purposes only the ordinary types of iron and steel are under consideration and any statements made, if not otherwise qualified, refer to such varieties. The Series 2 Experiments point to the conclusion that composition is not the determining factor in corrosion and that impure metal does not necessarily corrode faster than pure. In these experiments the external conditions obviously govern the rusting, and bring both impure and pure iron close together in final loss. Series 3 Experiments show the dominating influence of oxygen and air over composition in governing corrosion in the same kinds of metal. Further discussion of the influence of composition on corrosion will appear later.

(2) Physical Treatment

Under physical treatment are to be considered the various heat treatments, working the metal under heat, rolling and annealing, puddling, etc. Some of these treatments change the composition of the metal, others only its physical structure, or more important its surface, and corrosion, it may not be amiss to emphasize, is distinctly a surface phenomenon. There are occasions then, when physical treatment may be more important in influencing the commencement and course of corrosion than composition itself. Where deep pitting or slight but uniform general corrosion takes place its progress may be determined by so simple a factor as mill scale remaining closely adherent on certain parts of an iron surface only, and again corrosion may be prevented entirely for a long period of time by thin tightly adherent mill scale.

(3) Oxygen

Oxygen is shown in this paper to dominate over composition in determining the initial stages of corrosion and, acting through the medium of the products of corrosion, in determining more than any other single factor its entire course. Water is, of course, always assumed to be present either continuously or intermittently. It is possible that some corrosion results which have been reported as due to composition of the metal may have been due and perhaps determined by the physical treatment to which the metal has been subjected. On the other hand, atmospheric air or oxygen and particularly the products of corrosion are able to overbalance physical treatment as they are composition.

In this discussion as elsewhere, only the ordinary types of iron and steel are under consideration. In dealing with alloys of iron such as nickel-iron alloys and silicon-iron alloys and others, where in under ordinary circumstances there is little or no tendency toward corrosion, the same arguments will not apply or hold; but as pointed out above, the entire subject of corrodibility of series of iron alloys has not yet been undertaken.

(4) Products of Corrosion

The products of corrosion are themselves great accelerators of corrosion just as mill scale is. This accelerating action is due first

to the fact that the iron oxide formed during corrosion is strongly electro-negative compared to iron and when concerned in corrosion is always a cathode. Ferric oxide may also act as a depolarizer in corrosion since it is oftentimes reduced to Fe_3O_4. Its activity may be increased by condensation or adsorption of atmospheric oxygen on its surface although Friend believes his experiments have disproved this. It also acts by absorbing and holding water.

After the commencement of corrosion, its subsequent course is determined very largely by the physical character of the rust formed, its distribution over and its adhesion to the surface of the metal. It may so act as to stimulate general corrosion. It may be responsible for deep pitting or under other circumstances may retard corrosion or prevent it altogether for considerable periods at least, by close adhesion over considerable areas. It may cause corrosion to take different courses at different times, due to the fact that the rust formed at one time may be loose and wet, later on tightly adherent and later still dry and hard so that by the influence of moisture or temperature or physical strain it scales off from large surfaces, thus exposing the metal beneath and the cycle is thus renewed. Altogether rust appears to be the main feature of ordinary corrosion, not only as a result, but as a causative agent. Rust itself is dependent for its formation upon atmospheric oxygen with the slight assistance of carbon dioxide and its physical characters are developed chiefly by the conditions of corrosion as shown in another part of this paper. The behavior of the rust formed may also be dependent upon the physical treatment to which the metal has been subjected and to the composition of the metal, so that the conclusion appears warranted that composition of the metal, at least among the ordinary varieties of iron considered here, does not influence the progress of corrosion directly, but rather indirectly through the behavior of rust and the relationship of the rust to the metal composition and surface.

Thus the products of corrosion or rust act in a dull capacity, electrochemically as accelerators of corrosion and physically as a protective against corrosion. It is needless to point out that these two ways of functioning are diametrically opposed to one another and it can easily be imagined how many types of corrosion and peculiarities and apparently unexplainable differences in corrosion might be due to this fact alone. It is one of the purposes of this paper to indicate that many of the discrepancies in results previously reported

are due to the vagaries of the products of corrosion in influencing the progress of corrosion.

The Relative Importance of Composition, Oxygen and Iron Oxide in Influencing the Course of Corrosion

It is shown in this paper that under ordinary circumstances atmospheric oxygen dominates over the composition of the metal in inducing corrosion of iron and that the after course of corrosion is determined largely by the physical nature and adhesion of the products of corrosion which establish the principal electronegative areas on the metal surface. The relative importance of these three factors of corrosion and particularly the importance of composition is therefore of paramount interest. If oxygen determines the commencement of corrosion, and iron oxide and other products of corrosion determine its subsequent course, of what possible influence can the composition of the metal be? Composition of the metal is the one factor which can be more or less controlled for a given service. It is unthinkable that composition should not have some influence on corrosion. It is well demonstrated that irons containing much silicon, for example, do not corrode under ordinary circumstances and are very nearly insoluble in the common acids. Iron containing much nickel is also practically non-corrodible. Ordinary cast iron under many conditions corrodes less than steel or mild steel. These are well-known facts and our theories of corrosion must take them into consideration.

Apparently composition of metal does not influence corrosion directly, if we consider the ordinary varieties of iron and steel used in experiments of Series 2 and Series 4. However, the composition of the metal evidently does influence the course of corrosion profoundly in an indirect way through the influence of the products of corrosion. We have seen that the products of corrosion may behave in three different ways in influencing the course of corrosion:

1. The rust formed may fall or scale off.
2. The rust may be partially adherent and an accelerator.
3. The rust may be protectively adherent.

Naturally there may be also some intermediate stages between these three principal divisions. The physical and electrical behavior of the rust are dependent upon two factors:

1. The conditions under which the corrosion takes place.

2. The composition of the metal.

Thus, of two different metals of different compositions but subjected to the same circumstances as regards corrosion, the rust in the one case may act as an accelerator of corrosion and in the other may tend to act rather as a protective coating. In other words, the rust may tend to adhere less in one case and more in another, over smaller areas in one case and over larger areas in another, and thus under the same conditions, one metal will corrode more and another of different composition will corrode less.

The correlation between composition and the behavior of the products of corrosion on the basis of this theory of indirect influence of composition of the metal is most important, but requires a vast amount of work to bring it to a satisfactory and practical conclusion. If hydrogen is included as one of the products of corrosion, the phenomenon of polarization as a negative influence in corrosion should also be included; but, in this paper, by "products of corrosion" are meant the hydroxides, oxides and carbonates of iron produced during rusting in water and the salts and basic salts in salt solutions.

Corrosion of Polished Iron Surfaces

A perfectly polished iron surface consists of a film of pure iron spread over the entire metal surface and covering pure iron and impurities alike. The pure iron is apparently caused to flow in such a manner as to form a mirror-like film, under the influence of the polishing powder and the friction induced by the polishing mechanism, whether hand or machine. On such a polished surface of iron corrosion starts with some difficulty. Compared with ordinary smooth clean iron and more particularly with rather rough but clean surfaces, the polished surface offers more resistance to corrosion. It is also less easily attacked by acid. As is often found to be the case in metallographic work, when etching the polished specimens the higher the polish the more difficult it is to start the etching. Nevertheless if a drop of very pure redistilled water be placed on a highly polished iron or steel surface and allowed to dry, a spot of rust will be left. As a rule, the higher the polish the smaller will be the amount of rust remaining, and since samples of pure iron or steel take a higher polish than cast irons, the rust spot on polished cast iron is usually more prominent than on polished pure irons or steel.

If a piece of iron, cast iron or steel is rubbed to a smooth surface with fine emery cloth or similar abrasive and a drop of water applied, the water will flow over the surface and adhere tightly to the metal. Rusting begins immediately at numerous points. On the other hand, if the same metals are polished to a high degree with perfectly dry and grease-free abrasives, a drop of water instead of spreading over the surface rolls up into a spheroid as though in contact with an oily surface. If the metal is capable of taking a very high polish, rust formation begins slowly at a few points only and after the drop has dried only a small residue of rust remains, sometimes in the form of a narrow rim around the place where the drop stood. Less pure irons such as cast iron and semi-steel, which, as a rule, do not take as high a polish as pure irons and steels, also cause a drop of water to assume the spheroidal shape, but corrosion begins at numerous points and much sooner than in the other cases.

In such water-drop experiments the progress of corrosion can be followed by means of a microscope or hand lens, as the greenish-white ferrous hydroxide spreads outwardly through the water from the points at which the corrosion is occurring and gradually oxidizes to red rust. All of the samples of iron and steel used in Series 4 Experiments, described further on, were polished by means of dry abrasives as they would be for metallographic work, except that the polishing was carried to a higher degree, and a drop of water was placed on each. The rolled metals, consisting of copper-bearing irons, open-hearth pure irons, ordinary open-hearth and Bessemer irons, began to rust slowly from one or a few centers or nuclei and the total rusting as the drops dried did not amount to much. The puddled irons rusted more and from more centers. The cast metals, consisting of gray cast iron, semi-steel, white iron and malleable iron, rusted from numerous points, while the cast steels rusted from rather more points than did the rolled metals.

The principal difference between the rusting of the rolled metals and of the cast metals was in the number of centers or nuclei from which rusting proceeded. In the case of all the rolled metals the centers were few, in the case of the cast metals numerous, while the cast steels behaved more like the rolled metals. If after a rust spot has been formed on a well-polished surface of iron or steel, where in the first instance the rusting has proceeded slowly, another drop of water be so placed over the rust spot that it covers not only the spot but a portion of the unrusted polished surface as well, it is noticeable that

the water flows over and adheres readily to the rusted portion but, as before, not to the polished surface. The rusting now proceeds much more vigorously than in the first instance. Green ferrous hydroxide can be seen forming between and among the particles of red rust and also from the polished surface outside of the borders of the rust spot. It is noticeable that more rust forms from the polished surface near the rust spot than away from it. After the second drop of water has dried, greenish black areas are noticeable among the original grains of reddish rust and suggesting the possible origin of the magnetic oxide of iron formed under some conditions of corrosion.

After corrosion tests on polished surfaces, whether either pure water or the ferroxyl indicator in agar is used to cover an area of several inches square or more, it usually happens that there are more and larger electro-negative areas left with their original bright polish, on highly polished and comparatively pure samples than on less polished and comparatively impure samples.

The fact that the highly polished surface of iron starts to corrode more slowly than the less polished surface, such as that of cast iron or relatively less pure metal, might seem to hold out a faint hope that extreme purity of metal, if possible of attainment in a practical way, would be a means of reaching the much desired goal of corrosion-resisting iron. However, this hope does not seem warranted by the facts. Very pure open-hearth iron corrodes in the presence of oxygen more rapidly than cast iron. Electrolytic iron corrodes readily. Even highly polished surfaces corrode slightly in the beginning and after the first rust spot is formed, at an accelerated rate. So long as oxygen is the dominating influence which governs the commencement of corrosion, and rust and oxygen together control the subsequent course so largely, neither pure iron nor polished surfaces appear to offer the solution of the problem.

Passivity of Iron Considered as an Oxidation Phenomenon

When either commercial or electrolytic iron is immersed in strong oxidizing agents such as chloric, chromic or fuming nitric acids, or when touched with gold or platinum while dissolving in nitric acid of sp. gr. 1.35, or when heated momentarily in air, or when it is made the positive electrode in an electrolyte containing oxygen, it becomes passive and thereafter is not attacked by ordinary acids, no

longer precipitates copper, silver or lead from their salts and in general behaves like a noble metal.

All of these processes for producing passivity in iron are oxidizing processes.

Passive iron may be reactivated by heating in a reducing atmosphere, by the action of water, salt solutions, the diluted common acids, by making it the cathode in an electrolyte, and by other means.

All of the processes for reactivating passive iron are reducing processes, since hydrogen is disengaged in all of them, including contact with water and salt solutions, as in the ordinary process of corrosion in water.

Iron made passive either by fuming nitric acid or by chromic acid is electro-negative to ordinary iron, but the behavior of the passive surface in the two instances is somewhat different. The passivity conferred by chromic acid is more permanent apparently than that produced by nitric acid, which seems to be somewhat transient and evanescent. If a clean untreated strip of iron is tested against a strip made passive by nitric acid, in water acidulated with H_2SO_4, the circuit being completed through a sensitive galvanometer, at first the needle is strongly deflected in the sense that the untreated iron is positive to the passive iron, but suddenly the passivity leaves the treated strip, the needle of the galvanometer moves to 0, then it continues beyond and the current is reversed. This reversal persists for a long period of time. If a strip of iron be passivated by chromic acid the reversal of polarity occurs slowly and gradually in unacidulated water. However, if the test be made in water acidulated with sulphuric acid, the same general behavior is noted as in the case of nitric acid, and the depolarization and reversal of current take place with startling rapidity.

The same behavior and reversal of current occurs if mill-scale-covered iron is tested against iron made passive by chromic acid. At first the mill-scale-covered iron is positive to the chromic-acid-passivated iron but soon a reversal occurs. If nitric-acid-passivated iron is tested against mill-scale-covered iron (clean iron-held momentarily in the oxidizing flame) the nitric-acid-passivated iron is at first positive to the magnetic oxide. Later a reversal occurs, the mill-scale-covered iron becoming positive to the nitric-acid-covered iron. Sometimes when testing magnetic-oxide-coated iron against nitric-passivated-iron, the action starts with one strip neutral to the other, then suddenly the nitric-passivated iron becomes strongly positive

to the magnetic oxide. This gradually diminishes and the magnetic oxide becomes the positive pole and this reversal persists for a long time.

If two strips, the one treated with chromic acid and the other with fuming nitric acid be tested against each other through the galvanometer, they seem to be neutral at the beginning but very soon the nitric-acid-treated strip becomes positive to the chromic-acid-treated strip. The former has lost its passivity and again become active iron, which can be demonstrated by its action on nitric acid. These facts suggest but do not prove that there may be different degrees of passivity and that iron made passive by chromic acid assumes a higher degree of oxidation than that made passive by nitric acid. Furthermore, iron made passive by nitric acid appears to be of lower degree of oxidation than magnetic oxide of iron and the latter of a lower degree than iron made passive by chromic acid as judged by galvanometer tests and loss of passivity. The following electrochemical series suggests itself on the basis of these experiments and others reported in this paper:

+

Iron+adsorbed hydrogen (from acid).
Ordinary bright iron exposed to air.
Iron made passive by nitric acid.
Magnetic oxide of iron (Fe_3O_4).
Iron made passive by chromic acid.
Oxygen.

−

Ferric oxide (Fe_2O_3) is not placed in the above series and its exact position has not been determined. On account of its higher oxidation it should be more electro-negative than Fe_3O_4, but its relation to iron made passive by chromic acid has not been ascertained.

The explanation of the sudden reversals may not lie in successive degrees of oxidation as suggested by the electrochemical series given above. The reversals may be due merely to the fact that one type of passivity (including magnetic oxide passivity induced by the flame) becomes activated when connected in a circuit more speedily than another. However, there appears to be something more than this to the phenomena and direct and reversed currents appear to demand the above serial arrangement of the surfaces producing them.

In neutral salt solutions the first reversal of current occurs much

more slowly than in acidulated water, hours being required where seconds suffice in the presence of acid. In water also the same rule holds.

Although iron made passive by nitric acid and by chromic acid are both electro-negative to ordinary iron, this fact is not easily demonstrated by the use of the ferroxyl indicator, owing, no doubt, to the fact that when this indicator is applied hot in agar jelly, the passivity of the metal is soon lost. The ferroxyl indicator generally shows negative areas most promptly at the oxygen contact rim of the jelly, next at any rust spots, then where mill scale occurs. If the passivity could be retained, undoubtedly the appearance of red negative areas would correspond to the positions of oxygen, oxides of iron and passive areas according to the order shown in the above electrochemical series. It might be possible to develop a special ferroxyl indicator which would produce these results, but experiments have not been carried that far.

The oxide theory * of passivity apparently offers the best explanation and even though no actual oxides are formed on the surface of the iron, an equivalent gain in valence or loss of electrons can be visualized by the oxidation hypothesis, and suggests an interesting parallelism between passive iron and iron covered with mill scale and adherent rust. This parallelism may be stated as follows:

If all exposed pure iron surfaces in the crystallographic sense are uniformly covered by a layer of oxide either thin or thick, and if this film be tightly adhering, no corrosion takes place. A sub-microscopic film may be assumed to be produced over an iron surface by immersion in strong oxidizing agents such as chromic and nitric acids (the passive layer), a thicker and visible layer by an oxidizing flame (mill

* Dr. H. G. Byers does not accept the oxide theory of passivity, although he offers no substitute. Abstracts of his extensive investigations are found in C. A. 3, 274, 4, 1933, 6, 452, 7, 318, 7, 3268, 8, 3738, 10, 717. The original papers are as follows:

The Passive State of Metals. J. Am. Chem. Soc., 30, 1718–42.

The Influence of the Magnetic Field on the Passive State of Iron. J. Am. Chem. Soc., 32, 750–6.

The Influence of the Magnetic Field on Passive Nickel and Iron. J. Am. Chem. Soc., 33, 1757–61.

Passivity of Iron under Boiler Conditions. J. Am. Chem. Soc., 34, 1368–79.

Relation between the Magnetic Field and the Passive State of Iron. J. Am. Chem. Soc., 35, 759–67.

Passivity of Metals. J. Am. Chem. Soc., 36, 2004–11.

Anodic Relations of Passive Iron, with notes on polarization potentials as influenced by gas pressures. J. Am. Chem. Soc., 38, 362–74 (1916).

scale) and a more irregular and thicker layer during corrosion under certain conditions (rust). All three types of oxide layers protect against corrosion. However, if portions of such surfaces are removed by either physical or chemical means, corrosion starts at once, the abraded or dissolved areas becoming electro-positive and the oxide areas electro-negative. In all cases corrosion is prevented or delayed until the film of oxides is lifted or removed. Iron surfaced in any of these ways may in a very large and general sense be considered passive as regards corrosion in substantially the same sense, namely, by the uniform action of oxygen on exposed ferrite areas. There may be some doubt about the exact condition of the surface in passive iron induced by treatment with oxidizing agents, one view holding that the surface is simply polarized, another that it holds condensed or occluded oxygen and another that a sub-microscopic layer of oxide has been formed, but there can be no difference of opinion about oxygen being the active agent. In the case of iron surfaces coated with magnetic oxide, the nature of the protection against corrosion is obviously both electrical and mechanical. When such a protective layer of magnetic oxide is lifted from the iron surface in places by a film of water or is removed from certain areas mechanically, the remainder acts as an accelerator of corrosion and deep pitting generally results. This is also true for adherent rust. It probably would hold for passive areas provided these could be maintained in place for considerable periods of time.

Ferroxyl Indicator on Polished and Etched Surfaces

The initial rusting of a clean iron surface determines to a great extent the subsequent course of the rusting process. The first rust formed may be loosely or tightly adherent, may be more or less granular or in the form of a continuous film (depending on conditions), and as the rusting proceeds the rust formed will have or acquire different physical characters, depending on the composition or physical character of the metal affected and on the conditions promoting the corrosion. Any sort of iron oxide, including mill scale or iron rust, in close contact with any of the ordinary varieties of iron, stimulates corrosion unless it be in the form of a protective coating adhering closely enough to prevent contact of water with the iron beneath it and in any case profoundly modifies the course of the corrosion. If a drop of water be placed upon a clean surface of iron, cast iron or mild steel, or any of the ordinary varieties of iron, and

allowed to dry a spot of rust will be formed. If the entire surface of a clean piece of iron be moistened and if the surface be free from oil or grease so that the water spreads over it rather uniformly, certain irregular areas will be covered with rust and other areas will not—the rusting will not be uniform although the rust areas in some cases are large patches and in other cases very small, in the form of specks or flakes of rust. If initial rusting were guided and determined by the composition of the iron, one might naturally expect that the rusted areas would bear a definite relationship, when examined under the microscope, to the crystallographic structure of the metal and that if the corrosion took place under carefully regulated conditions that the ferrite areas would become anodes and produce rust spots corresponding to them in area, and that various segregated impurities in the iron would become cathodes and would remain bare of rust in the initial rusting, or until colloidal ferric hydroxide, moving with the electrolytic currents of corrosion, deposited on them. Nothing of this sort can be observed under the microscope, however carefully the rusting process is conducted.

In order to ascertain whether in fact ferrite areas are by their nature anodes and areas of impurities cathodes, in the rusting process, use was made of the very sensitive indicator developed by Messrs. Cushman and Walker and named by them ferroxyl indicator. Samples of all of the irons used for Series 4 corrosion experiments and listed in Table III were polished on the wheel in the ordinary way and slightly etched by nitric acid in alcohol. After the etching the acid was removed by immersion in successive beakers containing absolute alcohol and finally with ether. Different procedures were followed, some of the samples being dried after alcohol treatment and some after ether treatment. Duplicates were dried in the air and in hydrogen and various modified manipulations were made use of. Standard ferroxyl indicator in agar was dropped on the surfaces thus prepared and observations made by means of a microscope of moderate power. The crystallographic structure of the metal could be readily seen and the development of the blue and red areas in the jelly could also be followed. If initial corrosion were determined by the composition of the metal, the red and blue areas should bear a definite relationship to the crystallographic structure of the metal and it would be natural to expect blue areas to form only over ferrite areas and red over impurities of various sorts. However, the red and blue areas in no case bore any definite relationship to the crystallo-

graphic structure. By no manipulation which was used could red and blue areas be made to coincide with crystallographic areas. I do not wish to convey the impression that it would be impossible to refine the manipulation to such a degree that this correspondence might not be brought about, but in any of the manipulations adopted with any of the samples experimented on, it did not occur. Mild alkaline solutions were tried for the neutralization of acids used in etching, the alkali afterward being removed by absolute alcohol and ether and the drying being conducted both in air and hydrogen. But in this series of experiments the results were like the previous ones in that there was no correspondence between crystallographic areas and anode and cathode areas as indicated by the ferroxyl reagent.

Oxygen Dominates over the Composition of Metal in Initial Corrosion

All of the above experiments indicate what must have been thought by many experimenters on corrosion, that some influence dominates the composition of the metal in determining at what points or over what areas the initial corrosion may begin. This dominating influence in initial corrosion is undoubtedly oxygen. It may be oxygen which has been occluded or adsorbed by certain areas of the metal as opposed to other areas or it may be that some oxide or sub-oxide has been formed on certain areas in the form of an invisible film, but in any case the determining influence is oxygen whether free or in combination or held to the surface by occlusion or adsorption. That it dominates over metal composition in the initial stages of corrosion can be readily demonstrated by the fact that the red areas produced by the ferroxyl indicator extend over comparatively large surfaces, considered from the standpoint of crystallography, including very many ferrite crystal surfaces in the case of a mild steel or pure open-hearth iron. In instances where we might expect blue areas over ferrite we find red areas, and this occurs again and again in the experiments detailed above. The same observation holds for all the kinds of iron and steel, included in the Series 4 Experiments, including the cast metals. Oxygen then and not the composition of the metal should be considered the dominant factor in determining initial corrosion in the case of any of the ordinary varieties of commercial iron and steel.

It might be argued that the preliminary treatment of the polished samples such as the etching with an oxidizing acid, removal of the acid and the drying in air superimpose such conditions on the iron surface that certain comparatively large areas, at any rate larger than the crystallographic units, become electro-negative under conditions favoring corrosion. It should be noted, however, that while all the samples were etched by means of nitric acid, some of them were dried in oxygen and others in hydrogen. Etching, itself, by means of acid is a form of corrosion and on the basis of the accepted theory presupposes polarity on the polished surface. The etched surface would not be visible under the microscope were not certain crystallographic areas attacked by the acid and certain other areas left unaffected. Etching then follows the crystallographic structure of the metal, as would be expected, and if polarity is induced by the etching process, one would naturally expect that this polarity would also be definitely related to the crystallographic structure. We might assume that a given sample of polished iron or steel at the conclusion of the etching process would be in such condition that the subsequent corrosion under ordinary atmospheric conditions would be initiated in strict conformity with the crystallographic structure and the first corroded areas patterned after that structure. Whenever the corrosion takes place under atmospheric conditions or under water saturated with air, this is not the case. Hence again the conclusion seems warranted that some influence dominating over composition and structure of metal determines the initial course of corrosion and that this dominating influence is oxygen.

Why the oxygen of the air influences considerable areas to become electro-negative is difficult to say. An ordinary iron surface is a very sensitive one as regards corrosion. The slightest film of iron oxide over pure iron makes such an area electro-negative. Areas which appear tarnished and exhibit thin-film color phenomena are electro-negative with reference to non-tarnished areas. The tarnish probably consists of an extremely thin film of iron oxide or if the area has been in contact with acid, of an iron salt, probably a ferric salt.

Coupled with these facts is the one that passive areas produced on clean iron surfaces are electro-negative and that when such areas are produced by means of chromic or nitric acid there is practically no loss of luster and no visible change on the surface.

By the various means enumerated it was not found possible to cause the ferroxyl indicator to reproduce the metallographic pattern

of the various irons and steels used in Series 4 Experiments (and others) in red and blue. The question remains whether by the use of other etching solutions and by taking the greatest care to avoid the effects of oxidizing acids and other chemicals and of atmospheric oxygen, a surface might be produced which would give such a pattern. One cannot doubt the possibility and for the sake of the argument it may be assumed that under ideal conditions such a surface might be produced and that the reds and blues of the ferroxyl indicator would then conform to the metallographic pattern. However, the very difficulty of producing such an ideal surface and the ease with which its delicate equilibrium is upset by all sorts of agencies, chief of which under ordinary conditions is atmospheric oxygen, leaves the general argument unchanged and affords one more proof that composition of the metal, in the case of ordinary irons and steel does not determine corrosion in its initial stages, but on the contrary composition is easily overbalanced and dominated by oxygen and oxidizing agents as well as by the products of corrosion. Everything indicates that the ordinary clean iron surface is exquisitely sensitive to numerous influences affecting corrosion, chief among which under ordinary circumstances are oxygen and the oxides of iron or rust.

The Role of Oxygen

The importance of oxygen in the corrosion of iron was pointed out by William H. Walker as early as 1907 and was emphasized by him and others subsequently. Walker is of the opinion that when oxygen acts in such a way as to further the process of corrosion that it does so by its action on the hydrogen film which otherwise would bring the action to a close. That this action occurs and that it is catalyzed under certain conditions more than others cannot be doubted, for example, at the surface of certain metals and possibly iron, platinum, etc., more than other metals, but there is also the explanation that it may act simply and directly on the ferrous ions changing them to ferric and thus permitting more ferrous ions to enter the solution to restore equilibrium. At any rate this would seem to be an explanation which accounts for the marked difference in behavior under corroding influences in the absence and presence of oxygen of such bivalent metals as aluminium and zinc as compared with iron and manganese which are both capable of forming higher oxides and hydroxides. Air and oxygen do not accelerate the cor-

rosion of aluminium in the presence of water (as is shown in the experiments described toward the end of this paper) to any appreciable extent. It might be argued that this is due simply to the fact that the aluminium surface does not catalyze the oxygen-hydrogen reaction as does the iron surface. Against this we have the much greater solution tension of aluminium compared with iron. One volt for aluminium as compared with .06 for ferrous iron ($Fe^{\cdot\cdot}$). This explanation also has the advantage of agreeing with what actually and visibly occurs in corrosion experiments.

In the succeeding paper, "Rates of Solution of Iron and Steel," the relative difference between various samples of iron and steel dissolving in non-oxidizing acids such as hydrochloric and sulphuric and in oxidizing acid such as nitric are shown. Since the pure irons dissolve so slowly in non-oxidizing acids it was thought that if a current of oxygen were kept passing through the normal acid while the iron plate was suspended therein that solution would be accelerated. This was actually found to be the case but the increase was much less than anticipated. Evidently the oxygen was not brought close enough or in sufficient concentration, to the iron surfaces polarized by hydrogen.

The Role of Rust

Perhaps the most definite statements concerning rust as an accelerator of corrosion come from Friend.[1] He observes "When iron has once begun to rust in air, further corrosion proceeds rapidly, until the whole surface of the metal is oxidized, even although the temperature of the air is well above dewpoint, so that a piece of bright iron exposed in a similar manner would remain unaffected for an indefinite time." He rejects the suggestion of Kuhlmann[2] that rust acts as an oxygen carrier and thus catalytically assists further corrosion. He upholds the view held by Hutton, Crace Calvert, Wagner and Crum Brown to the effect that rust is decidedly hygroscopic and becomes charged with water in an atmosphere in which bright iron would not be affected.

Friend's experiments, however, to prove that rust does not act as an oxygen carrier may not be entirely conclusive. None of the experiments precisely correspond to rusting in air and in water.

[1] Corrosion of Iron and Steel, pp. 96–98, 252–253.

[2] Dammer, Handbuch der anorganischen Chemie, 1893, III, 303.

The results reported in Series 4 Experiments suggest that in some cases rust may act as a depolarizer and hence as an oxygen carrier.

Under condition 2 in which the plates were submerged in water, not agitated by air and taken out and dried semi-weekly, a layer of Fe_3O_4 formed next to the metal. This ferrosoferric oxide might have been formed by the reducing action of nascent hydrogen on Fe_2O_3 or by the combination of ferrous oxide (FeO) with ferric oxide (Fe_2O_3). Ferrosoferric oxide was also formed under other conditions.

Friend points out that the action of rust when iron is corroding in air and submerged in water may be different. In the latter case it acts as an accelerator on account of its electro-negative character.

Mill Scale vs. Ferric Oxide as an Accelerator

Mill scale as a rule causes deeper pitting than rust although ferric oxide, Fe_2O_3, on account of its higher degree of oxidation, should be more electro-negative than Fe_3O_4. The question naturally arises therefore, why does mill scale under ordinary circumstances act as a more powerful accelerator of corrosion? The answer is probably to be found in the different physical properties of the two substances as they usually occur. Ferric oxide is formed by dehydration of flocculent ferric hydroxide and is never as dense or as closely adherent as mill scale. The latter not only adheres closely but is very dense as usually formed by heat on the surface of iron and in addition is an excellent conductor. It is very difficult to obtain Fe_2O_3 of the same relative density and adhering to the surface in the same way as mill scale and it would be quite impossible to attain equal conductivity in the two substances.

Corrosion of "Busy Iron."

Engineers are unanimous in the belief that iron or steel in active service does not tend to corrode to the extent that idle iron or steel does; that the steel rail which carries many trains daily will outlast the rail carrying no trains; that the used hammer or other tool rusts less than the unused. The universal testimony of all observers indicates that their belief is well founded.

It may well be questioned whether there is anything intrinsical in use itself as affecting the metal physically, chemically or electrically, which would modify its corrodibility. The observed results are most likely due to surface changes induced by effects of service

and may be explained usually by one or more of the following consequences of continued use.

1. The polishing effect of hammering or rubbing which like all polishing actions produces a surface which resists corrosion.

2. The shaking or rubbing off of all but tightly adherent rust which in the end forms a protective layer.

3. The accidental coating of the surface of the used iron or steel with oil or oily substances during use which also prevents corrosion.

Cushman has suggested that continued vibration of iron or steel has the effect of equalizing potential differences and Friend believes that in the case of "busy rails" the passage of trains keeps them above the temperature of their surroundings and tends to prevent the condensation of moisture on their surfaces. Sang has suggested that "vibration causes a shedding of the rust, as soon as it is formed on the spots that are not protected by mill scale, and there is, therefore, no acceleration of the action due to the accumulation of spongy and electro-negative rust." Sang's explanation of one of the effects of vibration is undoubtedly correct as far as it goes and Friend's idea also is undoubtedly true but none of these explanations go to the bottom of the matter. There is no doubt that busy iron as a rule and continuously remains drier, under the same conditions of exposure, than idle iron, due to the cause which Friend has indicated in the case of rails, to vibration and in general to the conditions of use.

The used rail or old tool generally presents two surfaces: one, a polished surface, as the head of a hammer or the top of a rail, the other a dull surface covered with brownish black closely adherent rust, as the sides of a hammer or rail. The polished surface is naturally resistant to corrosion and the tightly adherent rust protects the iron under it. That neither type of surface rusts easily is a matter of common observation. Where these two types of surface join, there is however the likelihood of corrosion starting whenever suitable conditions arise, as when the iron or steel becomes idle.

When a railway rail remains idle for several hours during a rain the bright upper surface invariably becomes covered with rust but if trains are passing at frequent intervals the rust either is not formed at all or is quickly removed.

No more than a mere mention of oil on used iron is necessary. Casual reflection will indicate to anyone that the used tool or machine (or even the steel rail) when there is no intention of oiling it, is more likely to have oil dropped upon it accidently than the unused.

Perhaps a more correct statement than the usual one of the case of "busy iron" would be to say that (in the absence of oil protection) "busy iron" is protected on certain surfaces by polishing action but that on surfaces where it does corrode, it corrodes in a self-protective manner.

Series 4 Experiments

After the preliminary experiments of Series 1, Series 2 and Series 3 had been concluded it was thought that in view of the partial or the inconclusive nature of the evidence which they afforded that it would be best to start another series of experiments on a number of different varieties of iron which could be allowed to continue under the different conditions for a long period of time. It was hoped from the evidence which such a series would produce that some explanation might be forthcoming as to the reason for the difference between corrosion in acids, in water and under various conditions of service. Series 4 Experiments were the result.[1]

Kinds of Iron used in Series 4 Experiments

The varieties of iron and steel made use of in these experiments and their anaylses are given in Table 3. They included the nearly pure iron developed during recent years and manufactured by the open hearth process; ordinary open-hearth iron or mild steel; ordinary Bessemer mild steel; genuine puddled iron; charcoal iron; open-hearth iron containing a small amount of copper; grey cast iron; malleable iron; white cast iron; cast semi-steel and cast steel. All the samples measured 6 inches square, practically equivalent to 15 centimeters square. The rolled sheets were bought for No. 16 iron but some were a little light. The cast pieces were $\frac{1}{8}$ inch thick. The amount of surface exposed in the cast pieces, therefore, was slightly greater than in the case of the rolled sheets but in the tables this slight difference in the area has not been taken into account as it would have to be if all the figures were reduced to loss of weight from a unit surface, say 1 square inch. Samples of iron of the same kind from two different manufacturers were used in nearly every case. The exceptions were charcoal iron and Duriron of which one sample only was secured. Twenty-four plates, 6×6 inches of each kind were used.

[1] I wish to acknowledge especially the assistance of Messrs. J. DeRose, O. T. Bloom and L. S. Paddock in carrying out the experiments.

TABLE III

COMPOSITION OF IRONS USED IN SERIES 4 EXPERIMENTS

		Silicon. Per Cent.	Phosphorous. Per Cent.	Sulphur. Per Cent.	Manganese. Per Cent.	Total Carbon. Per Cent.	Graphitic Carbon. Per Cent.	Combined Carbon. Per Cent.	Copper. Per Cent.
AA	Copper bearing.....	.04	.007	.015	.063	.059	....	.059	.12
CC	Copper bearing.....	.03	.005	.016	.16	.056	....	.056	.10
BB	Open-hearth pure iron.	.04	.008	.015	.024	.030	....	.030	.015
II	Open-hearth pure iron.	.002	Trace	.019	.002	.020	....	.020	.023
JJ	Ditto cold rolled.....	.007	.002	.016	.023	.020	....	.020	.025
KK	Ditto cold rolled.....	.008	.002	.013	.020	.030	....	.030	absent
UU	Open-hearth iron.....	.008	.015	.043	.433	.164	....	.164	.021
WW	Open-hearth iron.....	.004	.020	.041	.282	.097	....	.097	.030
TT	Bessemer iron.....	.005	.075	.029	.450	.119	....	.119	.030
VV	Bessemer iron.....	.008	.025	.033	.407	.132	....	.132	.020
DD	Genuine puddled iron.	.14	.12	.014	.31	.023	....	.023	absent
EE	Genuine puddled iron.	.15	.17	.019	.030	.030	....	.030	Trace
XX	Charcoal iron.....	.003	.052	.013	.029	.060	....	.060	.047
FF	Grey cast iron.....	2.71	.82	.120	.32	3.21	2.62	.59	absent
SS	Grey cast iron.....	2.24	.40	.122	.44	3.08	2.67	.41	absent
LL	White cast iron.....	.81	.137	.054	.251	1.35	0.05	1.30	absent
OO	White cast iron.....	.48	.143	.044	.216	1.55	0.05	1.50	absent
MM	Malleable iron.....	.90	.134	.09	.25	.57	0.50	.07	absent
NN	Malleable iron.....	.77	.164	.067	.26	2.44	1.44	1.00	absent
GG	Semi steel.....	2.95	.92	.110	.33	3.06	2.72	.34	absent
RR	Semi steel.....	2.15	.327	.121	.46	3.15	2.35	.80	absent
PP	Cast steel.....	.26	.011	.024	.58	.20	....	.20	absent
QQ	Cast steel.....	.23	.036	.041	.58	.21	....	.21	absent
YY	Duriron.....	15.00	(approximately)						

All of the plates experimented on were used in their original condition with their surfaces untreated. Naturally they were all covered with mill or foundry scale except the cold-rolled sheets of pure open-hearth iron. The cast metals presumably had the usual cast metal surface which, as has been pointed out by others, may contain a comparatively high proportion of silicon and thus be more resistant to corrosion than similar metals which have been machined to remove the outer surface, but a reasonable doubt seems justified, that this influence amounts to much. The influence of surface, however, should be taken into account in all cases, although it will be seen from

an inspection of the results obtained with cold-rolled pure open-hearth iron as against the results obtained with similar metal rolled hot and covered with mill scale that the course of corrosion may be much alike under like conditions even when different surfaces are involved. The most noteworthy difference in the two cases is that the cold rolled metals subjected to the action of water agitated with air and dried semi-weekly showed a tendency for the rust to adhere more strongly than did the black iron.

The reason for not surfacing the plates was to ascertain the course of corrosion in the case of commercial metals with their ordinary finishes, unmachined and also unprotected by paint or other coating.

Conduct of Series 4 Experiments

All of the plates were subjected to eight different conditions:

1. Distilled water at rest.
2. Distilled water at rest, plates dried semi-weekly.
3. Distilled water with air agitation.
4. Distilled water with air agitation plates, dried semi-weekly.
5. 10 per cent salt brine at rest.
6. 10 per cent salt brine at rest, plates dried semi-weekly.
7. 10 per cent salt brine with air agitation.
8. 10 per cent salt brine with air agitation, plates dried semi-weekly.

One set of plates was allowed to remain submerged at all times while another set was removed from the water or brine and allowed to dry in the air semi-weekly, that is, the latter plates were hung in the air from morning until night on the days in question and then resubmerged. In all experiments three plates were used but it should be recorded that the difference in appearance between different plates from the same experiment and also the differences in weights at different periods was very slight.

All of the No. 4 experiments were carried out in the ordinary diffused light of the chemical laboratory and at ordinary room temperatures which for the most part ranged between 68 and 72° F. but might go occasionally to 90° F. in summer. The plates were suspended from wooden rods by means of strings attached through a single $\frac{1}{8}$-inch hole drilled near the upper edge of the plate. Six plates were hung from each wooden rod and 12 plates thus attached were placed in each of several earthenware jars measuring 15 inches in

diameter and 10 inches deep inside. The plates were kept submerged and water was added from time to time to replace evaporation losses. Whenever necessary the jars were emptied for the removal of flocculent rust and the plates replaced as promptly as possible in fresh water or brine. The air used for agitation came from the laboratory compressed air system (from a compressor) and no special means were used for washing it. The air was conducted to the bottom of the jars by means of a single glass tube and a moderately rapid stream of bubbles was kept passing through the liquid day and night, sufficient to agitate it slightly and keep it saturated. The agitation caused by the air may or may not have been an important factor in increasing the corrosion. Undoubtedly it did increase it to a certain extent since it is well-known that movement of the corroding plate or the solution is an important factor in corrosion, but how much increase of corrosion would be due to this factor must remain problematical.

Prior to weighing them, the plates were cleaned with an ordinary scrubbing brush which was sufficient for the removal of any flocculent or loosely adherent rust but which did not remove rust adhering tightly to the metal surface. At the conclusion of the experiments (1000 days) the plates were weighed after this method of cleaning, again after being cleaned with a stiff wire brush, and the cast metal plates, which were coated with a strongly adherent layer of rust and the W. R. D. series coated with magnetic oxide, a third time after sand-blasting. Thus the weights shown as 1, 2 and 3, respectively, in the tables and charts were obtained.

Before sand blasting was used as a means of cleaning the adherent rust and scale from the plates, careful experiments were made as to the conditions under which this removal could be brought about without actually taking off any appreciable amounts of the metal itself. Conditions were ultimately established which resulted in the removal of all the scale without the removal of enough of the metal beneath to affect the results. Prior to the adoption of sand blasting as a means of cleaning the plates, various other means were attempted but without success. One method was partially successful, namely, dipping the plates first in fatty acids heated to the smoking point followed by a rinse of hot water and immersion into boiling, strong caustic soda solution. This treatment removed rust and scale in some cases but was not by any means certain in its action. Hydrochloric acid and antimony trichloride in various proportions were

also tried but this means did not prove effective. Then the sand blast was applied.

All the experiments were continued for 1000 days with the exception of those plates which disintegrated and fell apart prior to that time. The charcoal iron plates corroded so rapidly that they were not experimented with beyond 500 days. An inspection of Chart XX will indicate that the rate of corrosion for the charcoal iron was very high.

After the cast plates were sand-blasted, the surface was ground off by means of an emery wheel, thus reducing the thickness of the plates somewhat and removing the silicon surface, if any. These plates were then replaced in water and brine and subjected to the same conditions as before. These experiments are now in progress. When completed, this series of experiments will furnish a comparison between the course of corrosion in the case of untreated cast-iron surfaces and cast iron with the original silicon surface removed.

The results of Series 4 experiments are recorded in Tables iv, v, vi, vii, viii and ix, and on Charts 1 to 23 inclusive.

Series 4 Experiments. The Brine Solution Used

The brine used was a 10 per cent solution of sodium chloride in distilled water made up from a pure grade of commercial salt and maintained at 10 per cent strength by suitable control periodically. Heyn and Bauer[1] and also Friend and Brown[2] have shown that the concentrated solutions of many salts (and inferentially perhaps most) are capable of reducing the amount of corrosion of iron or of inhibiting it altogether. These experimenters made use of one condition of corrosion only, and carried out their experiments by submerging the iron in a solution which was quiescent and whose surface was exposed to the air. The curves representing the results take peculiar forms. In many cases the curve rises for low concentrations only to fall with higher concentrations. In some cases there is a drop before the rise. Insofar as sodium chloride is concerned 10 per cent concentration is represented on the declining arm of the

[1] "Ueber den Angriff des Eisens durch Wasser und wasserige Lösungen," Mitteilungen aus dem königlichen Materialprüfungsamt, Berlin; 1910, **28**, 62; 1908, **26**, 2.

[2] "The Action of Aqueous Solutions of Single and Mixed Electrolytes upon Iron" read before the Iron and Steel Institute, London, 11 May, 1911. An excellent digest of Heyn and Bauer's experiments and also those of Friend and Brown may be read in J. Newton Friend's "The Corrosion of Iron and Steel," Chapter 9.

curve, thus indicating retardation of corrosion by this concentration. The fact that salt brine retards corrosion when iron is submerged and air only brought in contact with it by the slow process of diffusion from the surface the liquid is borne out in the Series 4 experiments but for other conditions, particularly when air is used for agitating the liquid and when drying is resorted to, the rule is not borne out. The results clearly show that brine is not the determining factor. Friend has shown that solutions of sodium chloride at ordinary temperatures and in the absence of air (oxygen) exert no appreciable action upon iron. If the results obtained under Conditions 1 and 5 detailed below are considered, the suspicion seems warranted that atmospheric oxygen is still the controlling influence since gases are generally less soluble in salt solutions than in pure water. If this is true and in the absence of reducing action by the salt or passivity phenomena supervening, one might expect the curves of Heyn and Bauer and Friend and Brown to follow the solubility curves for atmospheric oxygen in water and in salt solutions of increasing concentrations. When plates from the brine experiments of Series 4 are dried in the air, it follows that the concentration of the sodium chloride increases as the drying proceeds but in spite of the fact that when iron is submerged in quiescent solutions, the stronger brines reduce the corrosion, under conditions which provide an abundant supply of air corrosion in many cases proceeds more rapidly than when water is used. It seems quite evident that oxygen and rust are still the controlling factors whose influence is perhaps modified by the presence of sodium chloride in solution.

Appearance of the Series 4 Plates

After the Series 4 plates were removed from the corrosion experiments at 1000 days (500 days in the case of Charcoal Iron, Sample XX) their appearance was carefully observed. The detailed description of the plates is omitted in order to save space.

A certain uniformity in appearance prevailed in the case of all plates exposed to the same conditions of corrosion. For example, all of the plates under condition 1, water at rest, not dried, had a clean surface without mill scale or adherent rust. The same was true for condition 5, brine at rest, not dried. Under condition 3, water with air agitation, not dried, generally the surfaces remained clean. In some instances mill scale remained to the last and there was

a strong tendency toward pitting especially where mill scale had adhered or rust attached itself more firmly than usual. Condition 7, brine with air agitation, not dried, also preserved the surfaces clean as a rule and likewise showed a tendency toward pitting. Condition 2, water at rest, dried, left the surfaces covered with tightly adherent magnetic oxide of iron which in some instances produced fine pitting. Condition 6, brine at rest, dried, did not produce the magnetic oxide surface on the rolled metals but, on the other hand, the rolled plates under this condition were partly clean and partly covered with reddish brown rust. In some cases the surfaces were nearly clean and in numerous cases, especially among the cast metals, there was pitting action. Under condition 4, water with air agitation, dried, the plates were, as a rule, badly attacked. Some of the rolled sheets were corroded away entirely and the cast metals were frequently deeply pitted. In many cases deep pits and holes prevailed. Condition 8, brine with air agitation, dried, on the whole, perhaps, caused greatest corrosion in the majority of cases although condition 3, water with air agitation, not dried, also produce great losses. In the latter case (water with air agitation not dried) a clean surface was generally maintained throughout as noted above while the oxygen acted as a depolarizer. In the case of condition 8, brine with air agitation, dried, while adherent rust formed during the drying operation, this was lifted in some cases and removed by the brine, or perhaps it did not adhere closely enough to the metal to afford protection. At any rate the behavior of the adherent rust was decidedly irregular under this condition on the different samples.

Consideration of the Data of Series 4 Experiments

In considering the data of Series 4 Experiments as shown in the tables, on the charts or in the discussion, it should be emphasized that each result represents an average derived from three plates under each condition of the experiments and that each of the three plates revealed the same course of corrosion by appearance and quantitatively by loss of weight. There was no great difference either in the appearance of any of the three plates or their weights. Therefore, whatever it was in the conditions to which the plates were subjected, surface conditions, composition or physical treatment which produced the final results, these results were uniformly produced in all cases. There was nothing erratic in the behavior of

the individual plates. Whatever the causes contributing to corrosion in the various instances, it is evident that definite causes produce definite effects without any great variation in the final results or erratic behavior of individual samples.

The results of these experiments will be considered from two standpoints:

1. From the standpoint of the conditions to which the various plates were subjected.

This involves a comparison of the effects produced on different compositions of metal by like conditions of corrosion.

2. From the standpoint of the various kinds of iron and steel used in the experiments.

This involves a discussion of the different courses taken by corrosion when a metal of given composition is subjected to different conditions of corrosion.

Under the first heading emphasis will naturally be laid upon the similarities and differences developed under similar conditions and under the second heading emphasis will be laid on differences in the course of corrosion in the case of each metal experimented on under the various conditions of corrosion, due presumably to the action of oxygen and the products of corrosion under different conditions on the same kind of metal.

Explanation Tables 4 and 5

These tables give the results of Series 4 experiments under all the conditions.

Each figure represents an average of three separate plates measuring 6×6 inches. All rolled plates were bought for No. 16 iron and all cast plates were supposed to be $\frac{1}{8}$ inch thick. However, some of the rolled plates, notably the XX Charcoal Iron, were thinner and lighter as the original weights (O. W.) show. The puddled iron plates, EE, were nearly $\frac{1}{8}$ inch thick like the cast metal plates. All plates were carried for 1000 days except the charcoal iron plates. So many of these gave way at 500 days that all were removed.

Abbreviations

N. D. Not dried.
D. Dried in air semi-weekly.
O. W. Original weight.

L. Loss in weight.
1000–1. Loss in weight after brushing with fiber brush.
1000–2. Loss in weight after brushing with wire brush.
1000–3. Loss in weight after sand blasting. Only those plates were sand blasted which were coated with adherent rust which could not be removed by brushing.

TABLE IV

CORROSION OF IRON AND STEEL, SERIES 4 EXPERIMENTS.

LOSS IN GRAMS.

Age in Days.	Water at Rest.		Water Air Agitation.		10% Brine at Rest.		10% Brine Air Agitation.	
	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.
				AA COPPER BEARING				
O. W.	223.4	225.8	222.9	227.8	224.1	224.8	221.8	222.7
100L	4.0	5.5	24.1	38.7	2.1	9.7	14.4	27.3
200	6.6	9.3	37.2	56.3	4.3	19.9	23.6	54.9
300	8.1	12.2	48.8	72.6	5.1	27.2	34.6	78.7
400	9.8	15.2	71.0	90.3	6.9	37.8	47.9	107.2
500	12.0	17.5	88.8	105.3	8.4	45.5	55.8	124.8
600	13.8	21.2	101.2	125.4	9.8	52.8	61.9	147.8
800	17.9	27.0	138.5	156.1	13.4	80.2	87.2	192.1
900	....	....	....	....	....	....	....	All gone
927	....	....	....	All gone				
1000–1	22.7	31.2	177.5	....	17.4	110.8	110.6	
1000–2	22.7	31.2	177.5	....	18.0	131.1	110.6	
1000–3	22.7	45.9	177.5	....	18.0	131.1	110.6	
				CC COPPER BEARING				
O. W.	300.4	280.0	295.0	309.0	275.0	275.2	285.3	285.7
100L	3.6	4.0	19.0	19.4	1.7	2.7	11.9	16.4
200	6.4	6.7	34.7	32.8	4.9	10.8	24.0	36.8
300	8.8	9.2	50.8	51.0	7.7	32.9	36.2	69.0
400	10.8	11.9	67.0	68.0	9.8	49.8	51.6	94.4
500	13.3	14.5	83.9	86.8	11.7	60.2	63.2	119.2
600	14.7	15.8	105.8	103.7	13.2	70.6	72.9	141.9
800	18.7	19.3	144.2	119.8	16.5	92.5	88.7	214.1
945	....	....	....	....	....	....	....	260.0
1000–1	23.0	23.0	184.9	128.4	19.0	142.4	111.2	All gone
1000–2	23.0	23.0	184.9	172.3	19.0	153.9	111.2	
1000–3	23.0	36.8	184.9	204.2	19.0	153.9	111.2	

TABLE IV—*Continued*

LOSS IN GRAMS

Age in Days.	Water at Rest.		Water Air Agitation.		10% Brine at Rest.		10% Brine Air Agitation.	
	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.
BB OPEN-HEARTH PURE IRON								
O. W.	270.9	270.1	273.4	271.3	268.1	265.9	289.8	292.2
100L	2.9	2.2	17.2	11.9	1.6	1.7	13.3	19.5
200	5.7	3.4	31.5	20.9	4.5	3.5	24.1	33.3
300	9.2	6.0	44.0	39.7	8.6	20.1	39.5	72.2
400	12.3	7.3	59.9	55.9	10.1	22.1	52.1	98.4
500	15.2	9.3	75.6	66.3	12.6	32.5	64.5	124.4
600	18.8	10.6	104.1	72.9	14.2	53.9	74.1	141.9
800	24.2	13.1	139.6	84.6	18.4	83.0	97.0	239.0
945	....	....	....	....	....	....	....	264.2
1000–1	28.4	16.3	160.8	87.2	21.5	115.8	111.6	All gone
1000–2	28.4	16.3	160.8	129.7	21.5	145.7	111.6	
1000–3	28.4	51.2	160.8	164.8	21.5	145.7	111.6	
II OPEN-HEARTH PURE IRON								
O. W.	287.7	292.5	294.1	290.8	289.3	291.2	295.6	288.1
100L	3.0	3.3	15.1	17.5	2.6	9.9	12.4	22.8
200	6.0	5.1	24.4	26.1	4.7	18.2	21.6	42.1
300	8.7	6.3	39.3	34.5	6.1	31.8	32.5	62.3
400	11.8	8.2	53.1	42.1	8.4	42.3	45.7	85.9
500	14.4	9.4	74.8	48.3	20.0	54.7	56.3	107.3
600	16.2	11.0	92.6	56.4	21.1	62.8	56.4	126.6
800	22.5	13.0	124.0	71.1	24.9	96.9	73.6	197.1
1000–1	26.6	16.4	155.4	72.5	27.9	117.0	89.7	237.4
1000–2	26.6	16.4	155.4	102.1	27.9	133.5	89.7	247.9
1000–3	26.6	48.5	155.4	148.7	27.9	133.5	89.7	247.9
JJ OPEN-HEARTH PURE IRON								
O. W.	265.4	268.4	267.4	268.6	263.4	264.3	268.2	268.0
100L	2.0	2.2	17.2	11.1	1.9	10.1	13.8	22.7
200	3.6	2.9	36.9	19.9	2.9	19.5	27.1	44.1
300	5.6	4.5	56.2	27.4	4.7	28.3	40.3	64.2
400	8.2	5.2	75.7	29.9	5.8	42.8	50.8	83.6
500	10.9	6.7	98.4	31.1	7.8	49.5	69.1	95.9
600	13.3	7.9	118.9	31.1	9.6	57.8	84.0	110.5
800	18.6	11.6	167.5	32.6	11.7	86.6	112.2	190.5
1000–1	24.1	14.1	223.1	75.6	16.4	104.5	128.5	248.2
1000–2	24.1	14.4	223.1	92.5	16.4	107.2	128.5	253.0
1000–3	24.1	41.3	223.1	124.3	16.4	107.2	128.5	253.0

TABLE IV—*Continued*

LOSS IN GRAMS

Age in Days.	Water at Rest.		Water Air Agitation.		10% Brine at Rest.		10% Brine Air Agitation.	
	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.
				KK OPEN-HEARTH PURE IRON				
O. W.	241.3	238.9	239.6	241.2	243.3	242.0	241.0	239.4
100L	1.9	2.2	18.1	14.7	1.2	10.0	8.8	22.1
200	3.6	2.8	32.4	23.5	2.2	20.1	19.9	48.2
300	6.1	3.9	47.8	30.5	4.1	32.4	29.3	72.8
400	8.7	5.0	70.1	33.4	5.0	46.0	41.4	88.8
500	11.0	6.0	92.6	35.1	7.2	54.8	57.2	112.6
600	13.8	7.0	110.1	34.2	8.8	62.6	69.2	130.6
800	19.3	10.9	147.5	35.8	11.3	92.8	98.4	205.3
903	....	....	....	.....	....	....	....	222.9
1000–1	24.1	14.0	192.0	88.5	14.1	116.8	114.4	All gone
1000–2	24.1	14.0	192.0	106.2	14.1	129.2	114.4	
1000–3	24.1	41.5	192.0	132.7	14.1	129.2	114.4	
				UU OPEN-HEARTH IRON				
O. W.	299.3	283.6	284.0	282.4	281.9	289.8	287.3	295.0
100L	2.4	2.8	11.7	12.5	1.6	10.4	8.6	24.2
200	4.4	4.8	26.3	21.2	2.3	17.5	13.2	51.2
300	7.0	7.0	42.8	28.6	4.1	32.4	23.1	80.6
400	8.3	7.6	64.0	30.9	5.5	42.3	35.4	97.5
500	11.9	11.2	93.0	33.6	7.0	79.6	48.0	155.5
600	13.8	13.1	112.6	35.0	8.2	89.9	51.5	166.6
800	18.7	18.8	164.6	37.6	8.6	144.1	81.2	255.0
1000–1	21.3	23.2	188.6	112.3	12.2	173.5	95.9	All gone
1000–2	21.3	23.2	188.6	122.3	12.2	176.8	95.9	
1000–3	21.3	51.1	188.6	146.5	12.2	176.8	95.9	
				WW OPEN-HEARTH IRON				
O. W.	280.2	279.4	282.1	284.5	277.6	280.1	282.1	282.6
100L	1.3	.5	13.9	15.6	1.5	5.9	15.1	15.5
200	4.7	3.1	36.2	38.3	4.8	16.8	30.3	35.9
300	6.8	3.9	52.2	52.6	6.2	26.5	42.1	65.1
400	9.3	5.4	73.4	60.1	8.0	45.4	54.7	104.3
500	12.7	8.1	107.0	74.2	10.5	55.6	64.5	123.9
600	14.4	9.4	140.6	82.5	11.3	63.6	74.2	139.6
800	18.6	13.3	187.1	103.4	13.7	104.2	91.9	188.2
1000–1	23.8	19.0	215.5	183.5	15.9	140.3	102.3	219.3
1000–2	23.8	19.0	215.5	183.5	15.9	147.3	102.3	221.9
1000–3	23.8	49.9	215.5	186.6	15.9	147.3	102.3	221.9

TABLE IV—*Continued*

LOSS IN GRAMS

Age in Days.	Water at Rest.		Water Air Agitation.		10% Brine at Rest.		10% Brine Air Agitation.	
	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.
				TT BESSEMER IRON				
O. W.	289.1	288.3	287.5	284.8	285.5	286.2	285.1	279.4
100L	2.4	2.0	15.5	20.7	2.0	11.1	14.7	22.0
200	4.7	6.2	31.5	37.0	3.4	21.4	25.3	46.6
300	7.8	8.8	49.8	50.4	5.4	30.7	34.6	77.6
400	9.0	13.2	68.5	57.7	6.6	39.0	47.7	92.7
500	16.8	16.8	91.6	65.8	7.7	62.9	56.5	136.1
600	19.9	18.3	119.3	68.6	8.7	67.6	61.4	145.8
800	25.3	24.6	149.8	71.0	11.0	116.4	79.1	211.2
1000–1	29.5	28.5	178.4	144.7	14.1	158.4	96.8	247.2
1000–2	29.5	28.5	178.4	157.3	14.1	161.8	96.8	252.1
1000–3	29.5	53.5	178.4	171.0	14.1	161.8	96.8	252.1
				VV BESSEMER IRON				
O. W.	271.0	266.8	270.4	274.3	275.9	273.2	271.2	275.3
100L	1.9	1.0	26.5	19.6	2.2	8.1	12.2	15.2
200	5.1	2.9	44.8	39.8	5.4	21.3	34.1	38.3
300	7.5	4.0	58.1	50.1	6.4	31.4	46.9	67.0
400	10.0	4.6	81.8	57.5	8.7	56.4	53.5	104.9
500	13.0	6.8	107.5	64.1	10.5	72.3	65.4	123.3
600	14.1	7.8	151.1	69.3	11.6	80.1	74.4	141.9
800	18.2	12.5	207.8	77.5	14.7	131.0	88.0	192.9
1000–1	23.2	17.9	230.7	All gone	16.9	149.8	101.6	222.6
1000–2	23.2	17.9	230.7	....	16.9	153.8	101.6	222.6
1000–3	23.2	50.3	230.7	....	16.9	153.8	101.6	222.6
				DD PUDDLED IRON				
O. W.	270.5	275.6	276.0	297.7	274.3	268.6	276.3	276.3
100L	3.6	2.5	11.2	7.4	2.1	1.6	11.0	7.8
200	6.4	4.2	22.9	12.7	3.8	3.0	18.8	15.2
300	11.2	6.1	32.4	24.6	6.9	4.5	26.2	56.7
400	15.7	7.5	58.5	31.1	10.0	4.9	35.8	87.8
500	18.9	9.0	77.8	35.4	13.5	25.6	44.3	138.8
600	23.6	9.8	101.9	39.1	17.1	33.4	56.9	145.5
800	31.8	10.5	151.3	40.0	20.0	65.6	87.3	234.2
900	....	....	....	....	....	....	....	All gone
1000–1	39.1	11.4	194.9	41.7	24.1	80.7	102.1	
1000–2	39.1	23.4	196.6	103.8	24.1	151.9	102.1	
1000–3	39.1	65.6	196.6	143.1	24.1	151.9	102.1	

TABLE IV—*Continued*

LOSS IN GRAMS

Age in Days.	Water at Rest.		Water Air Agitation.		10% Brine at Rest.		10% Brine Air Agitation.	
	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.
				EE PUDDLED IRON.				
O. W.	646.2	638.7	640.1	640.9	640.3	638.9	638.6	640.5
100L	3.3	1.4	16.7	9.9	2.1	.6	10.6	6.1
200	6.4	2.3	33.7	13.1	4.5	1.6	21.9	11.2
300	11.3	3.6	59.4	17.8	6.9	1.6	33.5	31.9
400	16.1	4.8	78.8	21.6	9.2	2.0	47.2	42.6
500	19.1	6.1	106.1	19.3	10.8	2.4	56.9	83.4
600	24.1	9.4	139.7	19.9	14.5	2.7	72.5	89.1
800	30.4	15.2	192.6	18.5	18.2	3.7	92.8	105.8
1000–1	36.8	19.8	230.1	16.7	20.3	4.0	108.4	182.4
1000–2	36.8	21.6	231.6	73.6	20.3	92.0	108.4	292.7
1000–3	36.8	43.9	233.7	107.9	20.3	111.9	108.4	305.3
				XX CHARCOAL IRON				
O. W.	229.5	207.6	206.8	207.3	207.0	206.3	206.2	206.0
100L	4.8	4.6	30.1	27.8	3.7	8.7	15.2	23.1
200	9.7	9.5	56.8	57.5	5.0	20.1	26.7	50.0
300	14.2	15.3	87.8	88.4	8.0	51.6	40.6	93.6
400	17.9	19.4	123.8	106.1	9.8	52.7	53.5	110.3
500–1	21.6	22.7	152.9	165.1	11.4	60.8	70.6	138.3
500–2	21.6	22.7	152.9	189.4	11.4	90.6	70.6	160.3
500–3	21.6	33.8	152.9	189.4	11.4	90.6	70.6	160.3

YY DURIRON

Under all conditions Duriron failed to corrode except for a few flecks of rust which failed to produce a measurable loss of weight. The plates were however extremely brittle.

TABLE V

CORROSION OF IRON AND STEEL, SERIES 4 EXPERIMENTS.

LOSS IN GRAMS

Age in Days.	Water at Rest.		Water Air Agitation.		10% Brine at Rest.		10% Brine Air Agitation.	
	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.
				FF GRAY CAST IRON				
O. W.	759.1	787.4	750.8	743.0	737.8	771.5	769.0	766.3
100L	4.0	2.0	12.7	10.7	2.7	.0	7.9	13.4
200	6.1	3.3	24.3	11.0	3.8	3.8	15.2	21.9
300	8.6	4.3	42.8	11.4	5.6	.5	21.6	31.7
400	11.3	6.1	56.6	11.4	8.1	2.9	30.8	45.5
500	16.5	7.2	61.2	10.7	11.1	4.9	40.0	56.6
600	19.4	7.5	62.0	9.9	12.0	4.3	51.1	65.8
800	26.1	11.5	68.4	9.5	15.5	5.2	67.3	75.7
1000–1	31.1	13.2	78.8	8.4	19.9	5.1	81.1	81.8
1000–2	31.1	13.2	78.8	8.4	19.9	46.2	88.1	147.9
1000–3	31.1	24.4	78.8	62.9	19.9	95.0	88.1	196.6
				SS GRAY CAST IRON				
O. W.	700.0	696.5	682.2	753.3	687.1	802.0	780.0	749.9
100L	3.7	1.3	14.4	10.8	3.2	2.8	11.1	7.4
200	5.5	2.6	29.8	11.6	4.2	4.3	19.6	15.3
300	8.1	3.5	41.4	11.7	6.3	4.9	40.5	29.5
400	10.9	4.5	57.8	12.0	9.8	4.2	52.1	42.2
500	14.0	6.2	67.4	13.0	11.9	11.9	59.2	46.9
600	16.9	8.5	74.1	18.9	15.2	5.3	68.0	53.3
800	23.9	12.5	82.0	19.0	19.1	2.8	81.3	58.3
1000–1	28.6	15.1	103.4	20.5	22.3	1.9	90.8	66.6
1000–2	28.6	32.8	103.4	20.5	22.3	25.9	120.2	153.2
1000–3	28.6	32.8	103.4	42.0	22.3	57.2	143.5	195.5
				LL WHITE CAST IRON				
O. W.	733.3	772.6	752.3	765.0	787.2	750.6	784.5	756.4
100L	2.9	1.7	12.4	10.1	2.9	.9	14.9	9.0
200	4.2	2.1	32.4	13.7	7.0	....	21.8	12.9
300	6.8	3.1	49.1	15.3	13.6	....	30.5	16.9
400	10.2	4.7	69.5	15.5	14.7	8.6	43.1	27.7
500	13.7	6.0	86.0	15.7	18.2	10.8	54.8	40.0
600	17.9	9.3	105.2	16.8	20.6	11.5	65.3	46.9
800	21.9	10.6	133.8	15.5	22.0	11.6	75.3	55.7
1000–1	27.2	13.6	162.5	14.2	24.5	12.4	83.7	69.3
1000–2	27.2	13.6	162.5	14.2	24.5	24.2	83.7	73.5
1000–3	27.2	13.6	230.7	51.4	24.5	70.9	116.2	153.8

TABLE V—*Continued*

LOSS IN GRAMS

Age in Days.	Water at Rest.		Water Air Agitation.		10% Brine at Rest.		10% Brine Air Agitation.	
	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.
				OO WHITE CAST IRON				
O. W.	821.0	853.1	824.4	833.2	857.6	866.0	814.6	803.4
100L	3.5	1.7	11.2	9.7	2.8	1.0	8.7	5.2
200	5.2	2.4	23.7	15.8	3.7	1.8	16.8	12.4
300	8.6	4.1	50.8	19.0	5.3	.4	28.0	18.0
400	11.6	5.4	66.9	19.5	7.4	.8	38.4	27.8
500	14.8	7.9	88.2	19.6	9.5	1.9	44.2	45.1
600	18.8	11.0	83.1	28.0	13.6	1.9	54.1	46.6
800	24.2	16.8	87.4	26.6	15.6	2.9	64.3	57.4
1000–1	29.6	18.7	98.9	25.6	18.1	3.4	72.9	62.5
1000–2	29.6	18.7	98.9	25.6	18.1	9.3	72.9	68.9
1000–3	29.6	24.8	144.1	59.7	18.1	65.5	103.0	149.9
				MM MALLEABLE IRON				
O. W.	754.3	750.5	741.2	704.4	736.6	741.2	761.7	717.9
100L	2.9	1.7	12.5	9.5	2.2	.3	9.2	10.1
200	4.3	3.1	30.4	14.2	3.1	4.5	16.6	20.6
300	7.1	3.9	58.2	16.9	4.6	8.7	31.3	32.0
400	9.8	4.3	78.4	17.1	7.2	11.2	43.9	42.5
500	12.6	5.9	107.4	17.5	9.9	13.7	55.3	56.3
600	15.5	7.1	129.1	17.5	11.0	16.2	70.3	59.3
800	18.3	10.8	180.0	17.9	15.3	10.7	92.3	62.8
1000–1	23.8	14.8	215.2	18.6	17.8	31.7	118.5	95.6
1000–2	23.8	14.8	215.2	30.9	17.8	108.5	118.5	206.9
1000–3	23.8	31.6	222.2	63.1	17.8	130.2	118.5	237.6
				NN MALLEABLE IRON				
O. W.	825.8	791.1	858.6	828.1	811.3	854.3	826.8	821.5
100L	3.3	.7	13.5	6.5	2.4	.0	12.5	3.8
200	5.9	1.5	34.8	10.9	3.7	.8	20.7	17.2
300	9.8	3.9	61.0	14.3	6.6	1.3	33.6	28.0
400	11.7	5.3	81.0	14.4	10.1	2.2	51.2	38.1
500	15.3	7.1	110.1	14.5	11.5	1.1	57.1	53.0
600	19.5	11.1	122.6	22.6	14.0	2.3	71.3	58.2
800	24.0	15.0	165.8	22.9	17.2	6.7	92.3	68.7
1000–1	30.5	20.5	206.7	23.8	19.5	10.1	113.1	76.2
1000–2	30.5	20.5	206.7	34.8	19.5	79.0	113.1	154.4
1000–3	30.5	39.5	218.3	86.5	19.5	103.6	113.1	191.9

TABLE V—*Continued*

LOSS IN GRAMS

Age in Days.	Water at Rest.		Water Air Agitation.		10% Brine at est.		10% Brine Air Agitation.	
	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.
				GG SEMI-STEEL				
O. W.	739.9	817.0	756.8	763.7	762.9	771.8	769.2	762.8
100L	3.8	2.5	14.8	10.4	2.3	.0	8.7	13.9
200	6.8	2.8	32.1	10.6	2.7	4.5	14.8	24.6
300	10.4	5.7	40.4	10.6	5.3	4.2	21.9	36.2
400	14.1	7.6	49.3	8.9	8.2	1.6	31.2	53.3
500	19.6	9.3	54.4	8.5	11.2	1.1	44.2	63.5
600	22.7	11.0	56.2	7.6	13.2	1.1	53.1	71.7
800	27.7	13.4	58.5	12.2	16.5	1.3	69.6	80.8
1000–1	33.9	17.2	71.8	17.4	20.5	1.4	90.6	86.4
1000–2	33.9	17.2	71.8	17.4	20.5	36.2	95.6	151.8
1000–3	33.9	33.2	97.3	62.1	20.5	81.5	124.0	192.6
				RR SEMI-STEEL				
O. W.	737.6	780.6	716.6	739.3	775.0	707.5	746.0	738.7
100L	3.8	1.1	14.1	11.9	2.0	3.7	7.9	7.0
200	6.1	2.2	27.8	13.3	3.5	5.8	18.6	17.9
300	8.9	3.6	37.4	13.6	5.5	5.8	30.5	29.2
400	11.6	4.8	52.9	14.0	6.4	5.6	37.8	40.2
500	14.4	6.9	66.4	15.2	9.1	5.2	47.7	46.0
600	17.5	7.9	75.8	17.8	11.6	5.3	62.1	53.9
800	23.4	11.6	91.3	21.6	14.7	7.3	74.5	59.9
1000–1	28.8	15.6	118.6	23.7	18.5	8.8	85.0	68.2
1000–2	28.8	15.6	118.6	23.7	18.5	45.0	11.2	142.4
1000–3	28.8	25.2	118.6	48.1	18.5	81.4	124.5	189.2
				PP CAST STEEL				
O. W.	686.6	701.5	729.4	756.5	739.8	711.8	700.2	726.8
100L	2.2	.9	24.2	9.5	1.9	.0	10.9	3.7
200	6.4	2.7	45.2	20.1	5.0	1.7	18.7	17.5
300	9.5	3.9	70.4	24.0	7.4	1.7	30.2	68.3
400	14.2	4.9	107.3	25.2	10.0	.0	48.7	68.8
500	17.6	7.4	131.0	25.3	12.6	3.6	63.2	151.8
600	21.3	8.0	146.1	22.3	14.3	18.7	71.2	189.9
800	26.5	11.1	185.8	18.0	18.2	35.9	89.9	234.9
1000–1	30.6	16.7	235.0	15.5	18.8	47.2	97.6	274.1
1000–2	30.6	16.7	235.0	88.0	18.8	189.6	97.6	425.8
1000–3	30.6	55.5	242.2	120.7	24.4	218.0	107.4	447.7

TABLE V—*Continued*

LOSS IN GRAMS

Age in Days.	Water at Rest.		Water Air Agitation.		10% Brine at Rest.		10% Brine Air Agitation.	
	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.	N.D. Av.	D. Av.
				QQ CAST STEEL				
O. W.	587.5	646.5	616.0	640.5	651.7	621.8	635.8	621.5
100L	2.3	1.8	18.7	9.2	1.6	1.0	7.1	4.1
200	5.5	4.7	38.9	14.5	3.9	1.0	14.4	30.3
300	9.4	6.2	57.6	15.8	5.3	3.5	23.4	56.8
400	12.6	7.2	79.4	12.8	7.3	3.5	29.8	59.4
500	16.5	8.8	103.8	10.1	13.7	9.8	35.5	61.0
600	19.5	10.5	125.0	9.9	15.7	14.6	42.5	63.3
800	24.0	12.7	170.1	8.8	19.0	13.9	65.1	140.1
1000–1	29.2	17.0	240.8	9.1	20.3	22.9	70.1	149.0
1000–2	29.2	17.0	240.8	74.7	20.3	143.0	70.1	265.6
1000–3	29.2	36.2	247.6	122.3	24.9	160.3	78.5	285.9

CONSIDERATION OF THE RESULT OF SERIES 3 EXPERIMENTS FROM THE STANDPOINT OF THE CONDITIONS TO WHICH THE VARIOUS PLATES WERE SUBJECTED

The appearance of the plates under the various conditions was determined, generally speaking, by the conditions rather than by the kind of metal. While the experiments were in progress those under a given set of conditions appeared more alike, judging by the appearance of the surface, than unlike as they were known to be on the basis of composition. Certain corresponding sets in water and brine respectively also resembled each other. For example, the appearance of plates under condition 1 and condition 5 was very much alike, both showing fairly smooth, clean surfaces without pits. Other corresponding sets, although showing certain resemblances, still differed markedly as, for example, plates under conditions 3 and 7, water and brine respectively with air agitation. The plates in water for the most part showed pronounced evidence of pitting while those in brine did not. The deepest pitting was caused by local areas of strongly adhering mill scale in the presence of air and the next deepest by adherent rust in the presence of air.

All of the plates subjected to condition 2, water at rest, the plates being dried, become covered after a time with a coating of magnetic oxide of iron, Fe_3O_4 which in some cases could not be brushed or scraped off and finally required sand blasting for removal. The usual appearance of this coating was fairly smooth but dull and lustreless. This was true of all of the rolled sheets but among the cast metals were some in which this black layer did not adhere very strongly and this non-adherence resulted in its being lifted into small pimples at different points on the surface. In other cases the pimples broke or the black oxide was removed exposing the metal beneath which then became covered with the usual reddish rust and these same plates presented a mottled appearance, part black and part red. In still others the black oxide was removed altogether from time to time or did not adhere very strongly and these plates were covered with the ordinary red products of corrosion.

These and other details are discussed under the various headings below and are mentioned in this place merely to emphasize the fact that the conditions under which corrosion takes place dominated over composition in determining the course of corrosion in the common varieties of iron and steel, and that the influence of composition usually made itself felt indirectly by its effect on, or relationship, to the products of corrosion.

Condition 1, Corrosion in Water at Rest, Plates not Dried (Table VI).

In the case of a typical sample of rolled sheet metal covered with mill scale, corrosion starts wherever the mill scale is abraded, loosely adherent or porous. The corroding areas gradually enlarge and the mill scale is correspondingly reduced in area until it is finally removed. This leaves a rather smooth, finely crystalline surface and this surface is maintained throughout the experiment. Corrosion as measured by loss of weight proceeds at a very regular rate, the plotted losses producing nearly straight lines without appreciable irregularities. So far as oxygen is concenred in corrosion of this sort, it must enter the water by the slow process of diffusion and solution from the air. The rust formed is loose and flocculent and if at all adherent, easily removed by a soft brush. The losses in weight are, with one exception, greater than in the case of 10 per cent brine without air agitation and without drying. The single exception to this general

rule was furnished by Sample II, one of the samples of open-hearth pure iron, in which case the samples in brine lost slightly more weight than those in water. The corrosion in this instance shows a break between 400 and 500 days as though scale had formed and fallen off. This is the only instance of such an irregularity in any sample and whatever the cause, undoubtedly accounts for the results.

The cast metals behaved very much like the rolled metals but it is noticeable that on the average the losses from the cast metals were greater than in the case of the rolled metals. There is one exception to be noted, namely, the two samples of puddled iron which showed higher losses than any other rolled metal and also higher than any of the cast metals. It would appear from these results that when the ordinary types of iron and steel corrode under water at rest that the corrosion follows in general what would be expected from the electrolytic theory on the basis of composition apart from any marked influence by rust and that the more impure metals corrode most. Even this generalization, however, fails to hold good in particular cases. Thus, while the average loss from the cast metals at 1000 days is 29.4 grams and the average of the rolled metals with the exception of the puddled iron 24.6 grams, two samples of open hearth pure iron show greater losses than the average, whereas from their purity one might expect that they should show the least loss of all. Impurity is a general term, much too general, apparently, for the present discussion. Of the cast samples investigated the gray cast iron and the semi-steels contain more impurities than any others, these impurities being principally graphitic carbon and silicion. The impurities in the gray cast iron are greater than in the samples of semi-steel but the rate of corrosion is very nearly the same. One of the malleable irons is high in graphitic carbon and the other low. The one which is high in graphitic carbon shows a higher rate of corrosion than the one which is low in graphitic carbon. The two white irons although of similar composition showed different rates of corrosion, OO losing more weight than LL. Of the two semi-steels, the one containing the higher percentage of graphitic carbon and also silicion (GG) corroded more than the other (RR). The two cast steels are rather similar in composition except that one contains more phosphorus and sulphur than the other. However, the one containing the lesser quantities of these two ingredients corroded at a slightly higher rate than the other but the difference was not great. Thus it is not easy to arrive at generalizations in regard to corrodi-

bility as related to composition even in the simplest case of metals corroding under water in a quiescent state and hence with the influence of atmospheric oxygen reduced to a minimum.

Above all it should be emphasized that the most important distinction between this series of tests and the others is the absence of adhering rust. This is clearly indicated in Table VI, first three columns. If adhering rust were present the figures in column 3 would be greater than those in columns 1 and 2.

Condition 5—Corrosion in Brine at Rest, Plates not Dried. (Table VI).

Two principal points should be noted under condition 5, distinguishing the course of corrosion in brine at rest from that in water at rest. First, that with one exception the corrosion was less in brine than in water and second that adherent rust made its first appearance here although in the case of the cast steel samples only. It has been commonly supposed that brine and other electrolytes were necessarily accelerators of corrosion and there is evidence to support this view, particularly under atmospheric conditions when alternate wetting and drying occurs. At any rate this view has become current in spite of the demonstration of the contrary fact by Heyn and Bauer and Friend and Brown under such conditions that the iron was submerged in solutions of various strength, the only access of air being through the liquid surface. The results set forth in Table VI, condition 5 B. R. N. D., can perhaps best be explained by the fact that air and oxygen are less soluble in solutions of salt brine than in pure water. If oxygen is the determining factor in corrosion taking place under water and under brine, both in a quiescent state, the results could be explained by the relative solubility of oxygen.

In brine, puddled iron does not show the highest corrosion as it did in water but strange to say open-hearth pure iron does—that is, if we except the sample of charcoal iron which was continued for 500 days only and cannot be compared directly with the other samples.

As in the case of the samples under water, condition 1, the cast metals under brine, condition 5, show more corrosion than the rolled metal, the average losses in the former case being 20.1, those in the latter case (charcoal iron not being included) being 18.3. If the puddled iron samples are left out of the average of the rolled metals, the average figure becomes 17.5.

In considering corrosion under condition 1 and even more under condition 5, one is constantly reminded of the corrosion which takes place when iron dissolves in acids. The appearance of the plates is similar, that is, the surface is moderately smooth and the crystalline structure is in evidence. The pitting tendency is at a minimum. When metals dissolve in acids the liquid becomes saturated with hydrogen whereas under conditions 1 and 5, the liquids contain more or less atmospheric oxygen. This matter is more fully discussed under the heading "Dissolving of Iron by Acids."

TABLE VI

LOSSES AT 1000 DAYS. CONDITION 1, WATER AT REST NOT DRIED AND CONDITION 5, BRINE AT REST NOT DRIED.

1—Weighed as usual after light brushing. 2—After hard brushing with wire brush. 3—After sand blasting.

TEST		(1) W. R. N. D.			(5) B. R. N. D.		
Mark	Kind of Iron.	1	2	3	1	2	3
AA	Copper bearing	22.7	22.7	22.7	17.4	18.0	18.0
CC	Copper bearing	23.0	23.0	23.0	19.0	19.0	19.0
BB	Open-hearth pure iron	28.4	28.4	28.4	21.5	21.5	21.5
II	Open-hearth Pure iron	26.6	26.6	26.6	27.9	27.9	27.9
JJ	Ditto cold rolled	24.1	24.1	24.1	16.4	16.4	16.4
KK	Ditto silver finish	24.1	24.1	24.1	14.1	14.1	14.1
UU	Open-hearth iron	21.3	21.3	21.3	12.2	12.2	12.2
WW	Open-hearth iron	23.8	23.8	23.8	15.9	15.9	15.9
TT	Bessemer iron	29.5	29.5	29.5	14.1	14.1	14.1
VV	Bessemer iron	23.2	23.2	23.2	16.9	16.9	16.9
DD	Puddled iron	39.1	39.1	39.1	24.1	24.1	24.1
EE	Puddled iron	36.8	36.8	36.8	20.3	20.3	20.3
XX	Charcoal iron (500 days)	21.6	21.6	21.6	11.4	11.4	11.4
FF	Gray cast iron	31.1	31.1	31.1	19.9	19.9	19.9
SS	Gray cast iron	28.6	28.6	28.6	22.3	22.3	22.3
LL	White cast iron	27.2	27.2	27.2	24.5	24.5	24.5
OO	White cast iron	29.6	29.6	29.6	18.1	18.1	18.1
MM	Malleable iron	23.8	23.8	23.8	17.8	17.8	17.8
NN	Malleable iron	30.5	30.5	30.5	19.5	19.5	19.5
GG	Semi-steel	33.9	33.9	33.9	20.5	20.5	20.5
RR	Semi-steel	28.8	28.8	28.8	18.5	18.5	18.5
PP	Cast steel	30.6	30.6	30.6	18.8	18.8	24.4
QQ	Cast steel	29.2	29.2	29.2	20.3	20.3	24.9

Condition 3.—Corrosion in Water with Air Agitation, Plates not Dried. (Table VII).

The enormously increased corrosion which occurs on submerged plates when the liquid is kept saturated with air is prominently shown in Table VII. Generally speaking the results are less regular than in conditions 1 and 5, and are strongly suggestive of several influences at work leading to different final results in different cases. It might almost be concluded that the final results are to be considered as a compromise between different factors or a resultant of various forces acting in some cases in contrary directions. This will also be found to be true under the more drastic conditions of corrosion considered subsequently.

All of these samples show evidence of pitting action. In the rolled sheets this is due to a great extent to mill scale which adheres tightly in localized areas. Some of the rolled sheets, notably DD, Puddled Iron, were badly perforated with holes varying from $\frac{1}{8}$ inch to $\frac{3}{4}$ inch in diameter. The other sample of Puddled Iron, EE, while deeply pitted and suffering a greater loss, showed no perforations, the plates being somewhat thicker and the corrosion proceeding on the whole more uniformly over the surface. A few of the other samples of rolled metal show pitting and some great corrosion along the edges producing a deeply serrated or lace-like margin.

The cast plates also showed pitting but another prominent characteristic of these was the development of pimples, cones and craters on the surface. The formation of pimples was due to the separation of a film of oxide from the surface of the metal, presumably by gas. Underneath such a pimple a pit was formed. The cones and craters were formed in the usual manner by the movement of rust with the electrolytic currents as described by Cushman and Gardner.[1]

In general, the rolled metals show a more uniformly large amount of corrosion than do the cast metals. However, the two cast steel samples show the highest amount of corrosion of any. Among the cast metals are some which show the lowest rate of corrosion and of these one of the gray cast irons is lowest of all, one of the semi-steels being next. The average of the two samples of cast steel is 91.1 and of the semi-steel samples 108. Thus the two most impure metals of the entire lot show the least corrosion under condition 3. They also show no adherent rust.

[1] Corrosion and Preservation of Iron and Steel, Pages 57–61.

Obviously composition is not in itself and directly the determining factor here. Oxygen undoubtedly is, but with this fact admitted more light is needed on the behavior of the various cast metals, since they show such great variations in corrodibility, and also on the reasons for the rather uniform and high rate of corrosion in the rolled metals. The irregularities shown by the various metals under condition 3 and particularly when these results are compared with those obtained under condition 7 next to be considered, offer much data for careful consideration and suggestions for further experiments. The cast iron and semi-steel samples are the ones which suffered least corrosion and these metals are both distinguished by a high percentage of graphitic carbon and of silicon.

The failure of the gray cast irons and the semi-steels to corrode as rapidly as the purer rolled metals or the cast steels in the presence of oxygen but with rust for the most part absent, opens a wide line of questioning and tempts one to make hypotheses. Is it possible that we are dealing here with a mild form of passivity such as might be induced by the action of oxygen on the iron surfaces causing them to become electro-negative to the graphitic carbon? If we suppose the graphitic carbon in the cast metals to be electro-positive to oxides of iron, then possibly the ordinary direction of current under corrosion from iron to iron oxides would be modified and there would be no corrosion. In a succeeding paper the experiments on solution of iron in acids [1] show that nitric acid attacks the gray cast irons and semi-steels relatively less in comparison to the rolled metals than does a non-oxidizing acid such as sulphuric. In other words, solution in nitric acid is comparable to corrosion under condition 3 whereas solution in sulphuric acid is comparable to corrosion under condition 1.

To generalize and put the matter in brief form, the purer the metal the greater is the accelerating influence of oxygen and oxidizing agents (provided they do not induce passivity) in corrosion.

Condition 7.—Corrosion in 10 Per Cent Salt Brine with Air Agitation Plates not Dried. (Table VII.)

Under this condition all types of metal used showed less corrosion than under condition 3, with the exception of the two samples of gray cast iron and the two samples of semi-steel which showed greater corrosion under condition 7. However, even in the case of these two

[1] Rates of Solution of Iron and Steel in non-oxidizing and oxidizing Acids.

types of metal, the pitting action shown by practically all the plates under condition 3 was not in evidence. Generally speaking, all of the plates under condition 7 presented a fairly smooth, clean surface, finely crystalline in appearance in the case of the rolled metals and granular in the cast metals. The edges were not serrated and little mill scale or strongly adherent rust was present. In a few cases rust did adhere as indicated by the weights in column 3, but this was the exception. The difference in appearance between plates held under condition 3, compared with those held under condition 7 is striking, much more so than the difference in weights.

TABLE VII

LOSSES AT 1000 DAYS. CONDITION 3, WATER WITH AIR AGITATION NOT DRIED AND CONDITION 7, BRINE WITH AIR AGITATION NOT DRIED

1—Weighed as usual after light brushing. 2—After hard brushing with wire brush. 3—After sand blasting.

Test Mark	Kind of Iron.	(3) W. A. N. D.			(7) B. A. N. D.		
		1	2	3	1	2	3
AA	Copper bearing	177.5	177.5	177.5	110.6	110.6	110.6
CC	Copper bearing	184.9	184.9	184.9	111.2	111.2	111.2
BB	Open-hearth pure iron	160.8	160.8	160.8	111.6	111.6	111.6
II	Open-hearth pure iron	155.4	155.4	155.4	89.7	89.7	89.7
JJ	Ditto cold rolled	223.1	223.1	223.1	128.5	128.5	128.5
KK	Ditto silver finish	192.0	192.0	192.0	114.4	114.4	114.4
UU	Open-hearth iron	188.6	188.6	188.6	95.9	95.9	95.9
WW	Open-hearth iron	215.5	215.5	215.5	102.3	102.3	102.3
TT	Bessemer iron	178.4	178.4	178.4	96.8	96.8	96.8
VV	Bessemer iron	230.7	230.7	230.7	101.6	101.6	101.6
DD	Puddled iron	194.9	196.6	196.6	102.1	102.1	102.1
EE	Puddled iron	230.1	231.6	233.7	108.4	108.4	108.4
XX	Charcoal iron (500 days)	152.9	152.9	152.9	70.6	70.6	70.6
FF	Gray cast iron	78.8	78.8	78.8	81.1	88.1	88.1
SS	Gray cast iron	103.4	103.4	103.4	90.8	120.2	143.5
LL	White cast iron	162.5	162.5	230.7	83.7	83.7	116.2
OO	White cast iron	98.9	98.9	144.1	72.9	72.9	103.0
MM	Malleable iron	215.2	215.2	222.2	118.5	118.5	118.5
NN	Malleable iron	206.7	206.7	218.3	113.1	113.1	113.1
GG	Semi-steel	71.8	71.8	97.3	90.6	95.6	124.0
RR	Semi-steel	118.6	118.6	118.6	85.0	101.2	124.5
PP	Cast steel	235.0	235.0	242.2	97.6	97.6	107.4
QQ	Cast steel	240.8	240.8	247.6	70.1	70.1	78.5

It is noticeable that in general those samples of the cast metals which corroded most under condition 3 also corroded most under condition 7. Of the gray cast irons, SS corroded much more than FF in both cases and the white cast iron LL corroded more than OO; of the malleables, MM more than NN, and of the semi-steels, RR more than GG in water, but in brine the losses were much alike. The cast steels reversed themselves in a peculiar way under condition 7 compared with condition 3 and also showed a greatly diminished corrosion under condition 7. These comparative rates of corrosion are not casual or accidental. The appearance and the weights of the 3 different plates used in each case were very nearly the same. Although the influence of the composition apparently makes itself felt indirectly through the medium of oxygen and of rust, nevertheless the course of corrosion for a given metal is definite and not variable except as the conditions are varied. In this connection refer to the comparison between conditions 3 and 7 and solution in nitric acid shown in Table 11A.

Condition 2.—Corrosion in Water at Rest, the Plates being Dried Semi-weekly. (Table VIII.)

The characteristic thing about these plates was the tightly adherent coating of black magnetic oxide of iron which formed shortly after the mill scale came off and persisted throughout the experiment. The exceptions were not numerous. Among the rolled metals there were but two, namely, DD and EE, Puddled Irons. The surface in the case of DD was mottled red and brown, with exposed surfaces of iron showing through in small irregular areas of the darker rust. In EE the appearance was similar but with rather more of the black oxide in evidence. All of the other rolled sheets, including the charcoal iron, were uniformly covered with the adherent layer of black oxide. In some samples the pimples and blisters were more in evidence than others. The coating was as a rule uniform, of moderate thickness and with a dull, lustreless surface, which in some cases presented a pimply appearance.

The cast metals differed from the rolled sheets in showing a tendency in some cases toward the production of reddish or reddish-brown rust instead of the black magnetic oxide layer under condition 2, and on the other hand, toward the production of the black layer under condition 6. For example, the Gray Cast Irons, FF and

SS, showed reddish or red and black rust under condition 2 and black rust under condition 6. LL and OO, White Irons, and MM and NN, Malleable Irons, and GG and RR Semi-steels, all showed a tendency toward the production of black rust under condition 6. Most of these were also black or blackish under condition 2.

Apparently the black oxide forms underneath the red oxide and may be a reduction product of the latter, the reducing agent being electrolytic hydrogen, according to the following equation: $3Fe_2O_3 + 2H = Fe_3O_4 + H_2O$. Or it may be due to a combination of FeO with Fe_2O_3. The black oxide layer was observed occasionally under other conditions besides conditions 2 and 6 but to a less extent.

A glance at Table VIII indicates at once the comparatively small amount of corrosion in water as contrasted with brine, particularly in the case of the rolled sheets. Considering condition 2 by itself, a comparison of the figures in columns 1 and 2 indicates a rather adherent type of rust inasmuch as no more was removed in any case by rather severe brushing with a wire brush than by a soft brush. The average loss in the case of the rolled metals before sand blasting amounted to 20.7 grams and of the cast metals 16.2. After cleaning the plates by sand blasting, the average loss in the case of the rolled sheets was 41.1 and in the case of the cast metals 31.7. The black oxide appeared to cling much more tightly to the rolled metals than to the cast metals as a whole, in fact so closely that in most instances it appeared as though it had become a part of the metal itself and in sand blasting it was difficult to decide when the scale was entirely removed and the metal uncovered and how long the blasting should be continued for the removal of the oxide without affecting the metal beneath. There can be no question about this layer of oxide acting as a protective covering for the iron in these cases. (Compare condition 6.)

The two samples of cast steel, PP and QQ, behaved like the rolled metals and showed the black layer under condition 2 and reddish brown under condition 6, thus showing once more a similarity in corrosion behavior to the rolled metals which will appear again in several instances below. On the other hand, the gray cast-iron samples showed their unlikeness to the rolled metals and the cast steels in this instance as in others. The following table shows the different behavior of the various metals under conditions 2 and 6 as regards the production of black or reddish brown rust, judged by their appearance at the close of the experiment (1000 days).

		Condition 2. Water at Rest, Plates Dried.	Condition 6. Brine at Rest, Plates Dried.
AA	Copper bearing	Black	Fairly, clean, reddish
CC	Copper bearing	Black	Fairly clean, reddish
BB	Open-hearth pure iron	Black	Fairly clean, reddish
II	Open-hearth pure iron	Black	Fairly clean, reddish
JJ	Open-hearth pure iron	Black	Almost clean, reddish
KK	Open-hearth pure iron	Black	Almost clean, reddish
UU	Open-hearth iron	Black	Fairly clean, reddish
WW	Open-hearth iron	Black	Fairly clean, reddish
TT	Bessemer iron	Black	Fairly clean, reddish
VV	Bessemer iron	Black	Fairly clean, reddish
DD	Genuine puddled iron	Reddish	Red and brown
EE	Genuine puddled iron	Red and black	Red and brown
XX	Charcoal iron	Black	Red and brown
FF	Gray cast iron	Reddisn	Black
SS	Gray cast iron	Reddish	Black
LL	White iron	Black	Black
OO	White iron	Black	Black
MM	Malleable iron	Blackish	Brown black
NN	Malleable iron	Black	Brown black
GG	Semi-steel	Reddish	Brown black
RR	Semi-steel	Reddish	Brown black
PP	Cast steel	Black	Red brown
QQ	Cast steel	Black	Red brown

The cast metals differed from the rolled sheets in showing rather more red rust on the black oxide layer. On the cast metals the black oxide layer was not nearly so uniform as in the case of the rolled metals and was more intermingled with brown and red rust and was much rougher. There was also more evidence of pitting action, particularly in PP and QQ, the cast steels, and in MM and NN, malleable irons. The two samples of gray cast iron and of semi-steel showed little evidence of attack to the eye.

Condition 6.—Corrosion in 10 Per Cent Salt Brine at Rest, the Plates being Dried Semi-weekly. (Table VIII.)

The appearance of all of the plates under this condition was decidedly different from that under condition 2. The rolled sheets were not covered with the black oxide coating so characteristic of similar plates held under water and dried semi-weekly. Under

condition 6 the rolled metal plates remained partly clean and partly covered with a typical reddish brown rust. Much of the rust could be removed with a soft brush and practically all of it with a wire brush so that it was not necessary to resort to sand blasting. There was little pitting in any of the rolled sheets, the deepest occurring in the two samples of Puddled Iron, DD and EE. The charcoal iron showed no pitting.

Among the cast metals the most severe action occurred in the case of the two samples of cast steel, particularly PP and this action was evident to the eye in the form of broad deep pits and holes. Sample FF, Gray Cast Iron, showed slight pitting action while SS showed less. Samples LL and OO White Cast Irons, were both pitted but both lost much less weight than samples MM and NN, Malleable Irons. The iron losses were comparable to those of the gray cast irons and semi-steels. GG, Semi-steel, was uniformly pitted over the entire surface and presented a pock-marked appearance whereas RR showed larger areas of corrosion. Both, however, lost practically the same amount of metal. The average loss by the cast metals with the exception of the two cast steels was much less than the loss sustained by the rolled sheets. The two samples of cast steel lost an average of 189.1 grams, greater than that of any other sample. One sample of common open-hearth iron, UU, showed the greatest loss among the rolled metals, 176.8 grams, approaching the average of the cast steels and greater than QQ sample of cast steel.

The influence of the products of corrosion in causing pitting action and also in producing a protective coating is illustrated among the cast metals. The rust on the two samples of gray cast iron adhered very tightly as shown by the fact that these plates exhibited no loss in one case and only 2.1 grams in another when scrubbed with a soft brush. Treatment with a wire brush removed a considerable amount of rust and sand blasting a still larger quantity, although the final loss was comparatively low. The same holds true for the two samples of semi-steel. That the deposit of rust while moderately adherent was nevertheless softer and more porous in the case of the two samples of cast steel, is well shown by the three sets of figures shown for samples PP and QQ. Evidently in these cases there was a large amount of spongy or porous rust present which accelerated corrosion since it was not dense enough or closely adherent enough to protect the metal.

The two samples of semi-steel, GG and RR, and to a lesser extent

the two gray cast irons, FF and SS, showed a peculiar tendency to form a dry rust on their surfaces after sand blasting. These plates, as usual after the rust was removed by the blast, were wrapped in dry paper, as were all the others, and put away for a day or two in a dry room under exceptionally dry conditions of weather, etc. On opening the packages all were covered with a dry, powdery coating of reddish yellow rust. It was thought that this might have been due in some way to sodium chloride absorbed by the pores of the metal but the subject was not followed to a conclusion, as it had no significant connection with the principal line of experimentation.

TABLE VIII

LOSSES AT 1000 DAYS. CONDITION 2, WATER AT REST DRIED SEMI-WEEKLY AND CONDITION 6, BRINE AT REST DRIED SEMI-WEEKLY.

1—Weighed as usual after light brushing. 2—After hard brushing with wire brush. 3—After sand blasting.

Test Mark	Kind of Iron	(2) W. R. D.			(6) B. R. D.		
		1	2	3	1	2	3
AA	Copper bearing	31.2	31.2	45.9	110.8	131.1	131.1
CC	Copper bearing	23.0	23.0	36.8	142.4	153.9	153.9
BB	Open-hearth pure iron	16.3	16.3	51.2	115.8	145.7	145.7
II	Open-hearth pure iron	16.4	16.4	48.5	117.0	133.5	133.5
JJ	Ditto cold rolled	14.4	14.4	41.3	104.5	107.2	107.2
KK	Ditto silver finish	14.0	14.0	41.5	116.8	129.2	129.2
UU	Open-hearth iron	23.2	23.2	51.1	173.5	176.8	176.8
WW	Open-hearth iron	19.0	19.0	49.9	140.3	147.3	147.3
TT	Bessemer iron	28.5	28.5	53.5	158.4	161.8	161.8
VV	Bessemer iron	17.9	17.9	50.3	149.8	153.8	153.8
DD	Puddled iron	11.4	23.4	65.6	80.7	151.9	151.9
EE	Puddled iron	19.8	21.6	43.9	4.0	92.0	111.9
XX	Charcoal iron (500 days)	22.7	22.7	33.8	60.8	90.6	90.6
FF	Gray cast iron	13.2	13.2	24.4	5.1	46.2	95.0
SS	Gray cast iron	15.1	15.1	32.8	1.9	25.9	57.2
LL	White cast iron	13.6	13.6	13.6	12.4	24.2	70.9
OO	White cast iron	18.7	18.7	24.8	3.4	9.3	65.5
MM	Malleable iron	14.8	14.8	31.6	31.7	108.5	130.2
NN	Malleable iron	20.5	20.5	39.5	10.1	79.0	103.6
GG	Semi-steel	17.2	17.2	33.2	1.4	36.2	81.5
RR	Semi-steel	15.6	15.6	25.2	8.8	45.0	81.4
PP	Cast steel	16.7	16.7	55.5	47.2	189.6	218.0
QQ	Cast steel	17.0	17.0	36.2	22.9	143.0	160.3

Condition 4.—Corrosion in Water with Air Agitation, the Plates being Dried Semi-weekly

This condition and the succeeding one, No. 8, in which brine is substituted for water, were the most drastic of all utilized in Series 4 Experiments. As a consequence the losses were higher than under the conditions previously considered. All samples were more or less covered with reddish brown rust. In some cases this was tightly adherent in spots. In others it was spongy. The rolled metals under condition 4 were much more severely attacked as a whole than the cast metals, the only cast metals approaching them in pitting effect and general corrosion being the two samples of cast steel.

Of the two copper-bearing mild steels, one, AA, was destroyed altogether, that is, it was so badly pitted and corroded that there was not enough metal left toward the last to permit of its being continued in the experiment whereas CC, while badly pitted and suffering from general corrosion held together much better. This is an interesting case since the composition of the two kinds of metal is very much alike. Nevertheless, due to some unknown factor (possibly physical treatment) one suffered from corrosion and disintegration much more than the other. Needless to say both would have failed in service long before 1000 days. The losses of the copper-bearing metals were greater than those of any other samples of rolled metal under condition 4.

Samples BB and II, representing typical open-hearth pure irons, presented an almost identical appearance, being badly pitted and full of holes, but in Sample BB the corrosion was obviously greater and the loss is greater too. Samples JJ and KK, representing cold rolled open-hearth pure irons, suffered considerably less loss than the two black samples, probably owing to the accelerating effect of mill scale in the latter cases and to the protective action of rust which adhered more tenaciously in the former. The samples of ordinary open-hearth iron, UU and WW, on the average lost somewhat more weight than samples BB and II and sample WW in particular did not hold together so well. Sample UU, however, at the end of the experiment presented a better appearance than either BB or II and was less pitted and showed fewer holes. On the other hand, WW exhibited weaknesses apparently due to uneven composition or bad mechanical treatment. The two samples of Bessemer Iron, TT and

VV, did not do as well as the open-hearth samples, VV being entirely gone before 1000 days, although its true condition was concealed during most of the experiment by adherent rust. These two samples (TT and VV) afford an interesting contrast. TT was badly attacked as shown by loss of weight whereas VV, judged by loss of weight during the course of the experiment, showed scarcely greater losses. Both were rather heavily coated with rust, but the processes of corrosion had gone on under the rust covering of VV to a much more insidious extent than under the rust of TT so that at the end of the experiment sample VV crumbled away while TT still retained enough metal to hold it together. The Bessemer TT did better than Open Hearth WW. The puddled iron samples did rather well, sample DD comparing favorably with the pure open-hearth samples BB and II. EE presented a still better appearance and in fact showed the lowest loss of any of the rolled samples under condition 4. The charcoal iron was practically disintegrated before 500 days.

Of the cast metals, all but the two cast steels held up in a remarkable manner throughout the test although all showed evidence of pitting action. The two best in appearance were the two gray cast irons with the two semi-steels running a close second. The white irons and the malleable irons were about alike in appearance although the malleable samples lost more than the white irons. The two cast steel samples lost more than any other of the cast metals but less than most of the rolled sheets. They were, however, badly pitted and showed every evidence of the worst sort of corrosion such as results in early failure.

Condition 8.—Corrosion in 10 Per Cent Salt Brine with Air Agitation, the Plates being Dried Semi-weekly. (Table IX.)

Judging by the appearance of the plates and the losses, this was the severest condition of all. As in condition 4, all plates were covered with reddish brown rust which showed different degrees of adhesion in the case of different samples. Speaking of all the plates, the chief difference perhaps between those from condition 8 and condition 4 was the larger pits and holes produced in condition 8.

Several of the rolled sheets were entirely disintegrated before 1000 days. The sample that stood the test best of all was WW, one of the ordinary open-hearth irons, with VV, Bessemer, a close second. Two of the three plates in this case (WW), while very thin, showed no

deep pitting action. The third was more severely attacked and exhibited pits and holes. Samples AA and CC, the copper-bearing metals, were entirely disintegrated although CC lasted longer than AA. Of the two black open-hearth pure irons, BB and II, the former was entirely gone and the latter nearly so. Samples JJ and KK, the cold rolled open-hearth pure irons, were entirely disintegrated, both disappearing about the same time. Of the two common open-hearth irons, UU was entirely disintegrated but WW persisted and while thinner than the duplicate sample in water was more uniformly attacked and less pitted. Of the two Bessemer samples, while both were badly attacked, VV shows less loss in weight than TT. Sample DD, puddled iron, was entirely disintegrated prior to 1000 days, EE being thicker and also because corroding less, lasted through the experiment and while badly corroded showed less pitting action than some other samples. The fibrous structure of the metal, however, was emphasized by the corrosion, the pits running longitudinally and parallel with the fibres. Sample XX, charcoal iron, showed less loss in brine (condition 8) than in water (condition 4).

The cast metals were all pitted with deeper and wider pits than under condition 4 Sample FF, Gray Cast Iron, was perforated in several places whereas Sample SS while suffering practically the same loss was not. The two samples of white iron showed the lowest losses of any sample. MM and NN, Malleable Irons, were about equally attacked, judging by appearances, but in different ways. MM was more deeply pitted whereas the edges of NN were badly corroded. GG, Semi-steel, was deeply pitted and at a number of points perforated but RR, Semi-steel, while losing about the same weight was not so severely attacked locally. Of the two cast steels, PP was very severely attacked, being perforated with large holes and exhibiting wide and deep pits. The pits in QQ were also very wide, but there were fewer perforations and the loss of metal was much less in this case.

It is a most difficult matter to draw any conclusions from these experiments which correlate composition and corrosion. Gross mechanical and physical differences undoubtedly invite corrosion as can be seen by inspection of the cast metals, but on the other hand extreme purity and uniformity (in the sheet metals) do not protect against corrosion. The less pure metals on the whole resisted corrosion under condition 8 better than the purer, the best samples being in order the white cast irons (average loss 151 grams), the semi-

steels (average loss 191 grams) and the gray cast irons (average loss 196 grams). Malleable Iron MM with the lower carbon content lost much more (237 grams) than NN with the higher carbon content (192 grams). This is what would be expected from a comparison of the cast and rolled metals in respect to carbon content.

TABLE IX

LOSSES AT 1000 DAYS. CONDITION 4, WATER WITH AIR AGITATION, DRIED SEMI-WEEKLY AND CONDITION 8, BRINE WITH AIR AGITATION, DRIED SEMI-WEEKLY.

1—Weighed as usual after light brushing. 2—After hard brushing with wire brush. 3—After sand blasting.

Test Mark	Kind of Iron	(4) W. A. D.			(8) B. A. D.		
		1	2	3	1	2	3
AA	Copper bearing	All	gone		All	gone	
CC	Copper bearing	128.4	172.3	204.2	All	gone	
BB	Open-hearth pure iron	87.2	129.7	164.8	All	gone	
II	Open-hearth pure iron	72.5	102.1	148.7	237.4	247.9	247.9
JJ	Ditto cold rolled	75.6	92.5	124.3	248.2	253.0	253.0
KK	Ditto cold rolled	88.5	106.2	132.7	All	gone	
UU	Open-hearth iron	112.3	122.3	146.5	All	gone	
WW	Open-hearth iron	183.5	183.5	186.6	219.3	221.9	221.9
TT	Bessemer iron	144.7	157.3	171.0	247.2	252.1	252.1
VV	Bessemer iron	All	gone		222.6	222.6	222.6
DD	Puddled iron	41.7	103.8	143.1	All	gone	
EE	Puddled iron	16.7	73.6	107.9	182.4	292.7	305.3
XX	Charcoal iron (500 days)	165.1	189.4	189.4	138.3	160.3	160.3
FF	Gray cast iron	8.4	8.4	62.9	81.8	147.9	196.6
SS	Gray cast iron	20.5	20.5	42.0	66.6	153.2	195.5
LL	White cast iron	14.2	14.2	51.4	69.3	73.5	153.8
OO	White cast iron	25.6	25.6	59.7	62.5	68.9	149.9
MM	Malleable iron	18.6	30.9	63.1	95.6	206.9	237.6
NN	Malleable iron	23.8	34.8	86.5	76.2	154.4	191.9
GG	Semi-steel	17.4	17.4	62.1	86.4	151.8	192.6
RR	Semi-steel	23.7	23.7	48.1	68.2	142.4	189.2
PP	Cast steel	15.5	88.0	120.7	274.1	425.8	447.7
QQ	Cast steel	9.1	74.7	122.3	149.3	265.6	285.9

Consideration of the Results of Series 4 Experiments from the Standpoint of the Various Kinds of Iron and Steel used in the Experiments

Having considered the results of Series 4 Experiments from the standpoint of the conditions to which the plates were subjected, the various kinds of metal will now be taken up individually and the course of corrosion followed under the various conditions for each one. Reference should be had to the charts Nos. 1 to 23, inclusive. The following abbreviations are used on the charts for the conditions to which the metals were subjected:

Condition.	Abbreviation.
1. Water at rest, not dried	W. R. N. D.
2. Water at rest, dried	W. R. D.
3. Water, air, not dried	W. A. N. D.
4. Water, air, dried	W. A. D.
5. Brine at rest, not dried	B. R. N. D.
6. Brine at rest, dried	B. R. D.
7. Brine, air, not dried	B. A. N. D.
8. Brine, air, dried	B. A. D.

Where figures are used in connection with initials such as W. A. N. D. 1, W. A. N. D. 2, W. A. N. D. 3, these refer to weighings made respectively after cleaning the plates with a soft brush (1), after cleaning the plates with a stiff wire brush (2), after sand blasting so as to remove all products of corrosion (3).

Copper Bearing Irons—AA and CC. Charts 1 and 2

These samples represent copper bearing metals made by two different manufacturers. As shown by the analysis the composition is very similar, the greatest difference being in the manganese content. The copper content is very nearly the same, 0.12 per cent in AA and 0.10 per cent in CC. In order of corrodibility under the various conditions these two samples stand as follows:

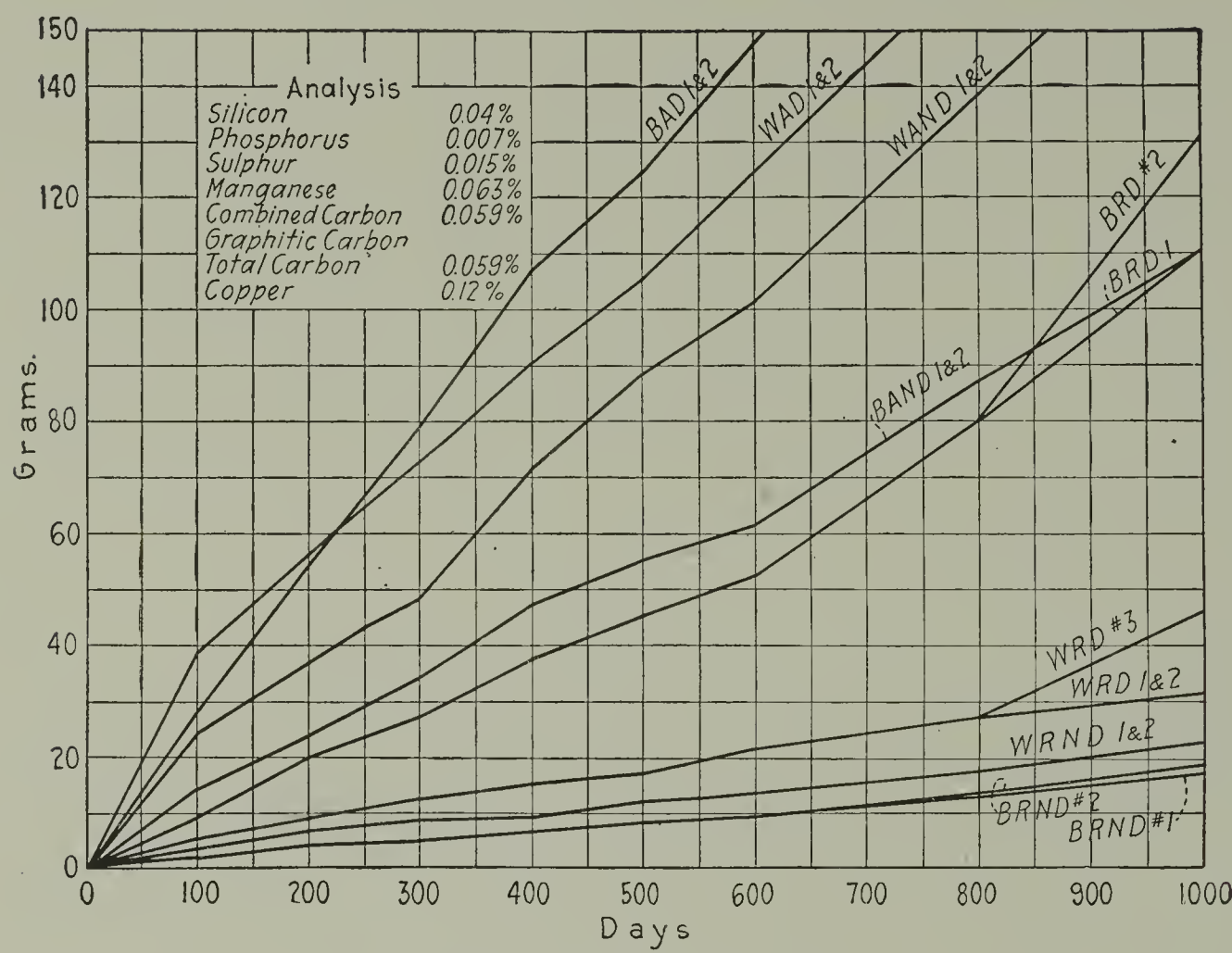

CHART 1.—AA Copper Bearing.

AA	CC
Least	Least
5. B. R. N. D.	5. B. R. N. D.
1. W. R. N. D.	1. W. R. N. D.
2. W. R. D.	2. W. R. D.
7. B. A. N. D.	7. B. A. N. D.
6. B. R. D.	6. B. R. D.
3. W. A. N. D.	4. W. A. D.
4. W. A. D.	3. W. A. N. D.
8. B. A. D.	8. B. A. D.
Most	Most

Under condition 5, B. R. N. D. and 1, W. R. N. D., the corrosion is relatively slight and the figures run close together, although there is definitely less corrosion in brine than in water. When the plates were kept submerged in water under condition 2, W. R. D., and dried semi-weekly, more corrosion took place but under all three of these conditions the corrosion was much less than under the five others. Under condition 7, B. A. N. D., and 6, B. R. D., the corrosion was much greater. The B. R. D. plates developed a coating of rust which when removed reduced the weight below that of the

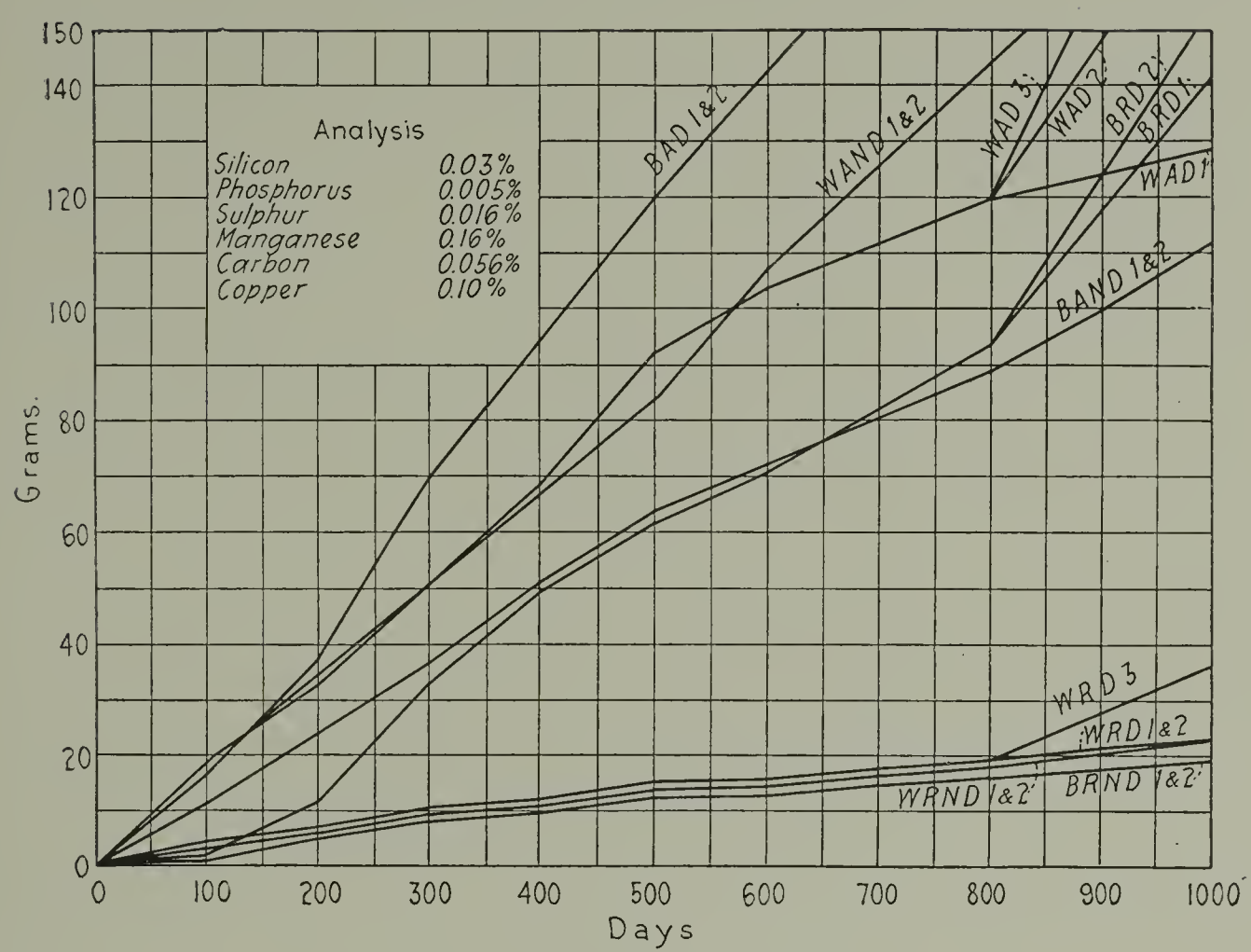

CHART 2.—CC Copper Bearing.

B. A. N. D. plates which naturally did not develop a coating of adherent rust. The amounts of corrosion under condition 3, W. A. N .D and 4, W. A. D., are reversed in the two samples, AA showing the greater corrosion under condition 3, W. A. N. D., and CC. under condition 4, W. A. D. In both samples, condition 8, B. A. D., produced the greatest amount of corrosion. Although the plates were dried in this case the rust did not adhere and the surface was for the most part clean. On the othr hand, the corresponding plates in water, condition 4, W. A. D., in both cases show by their curves unmistakable evidence of adherent rust. For this reason in the case of AA the curve of W. A. D. crosses that of B. A. D. at about 230 days and in the case of CC crosses the curves of both B. A. D. and W. A. N. D. even after sand blasting (W. A. $D._3$).

As regards pitting action the following order prevailed:

AA	CC
1. W. A. N. D.	1. W. A. N. D.
5. B. R. N. D.	5. B. R. N. D.
6. B. R. D.	6. B. R. D.
7. B. A. D.	7. B. A. D.

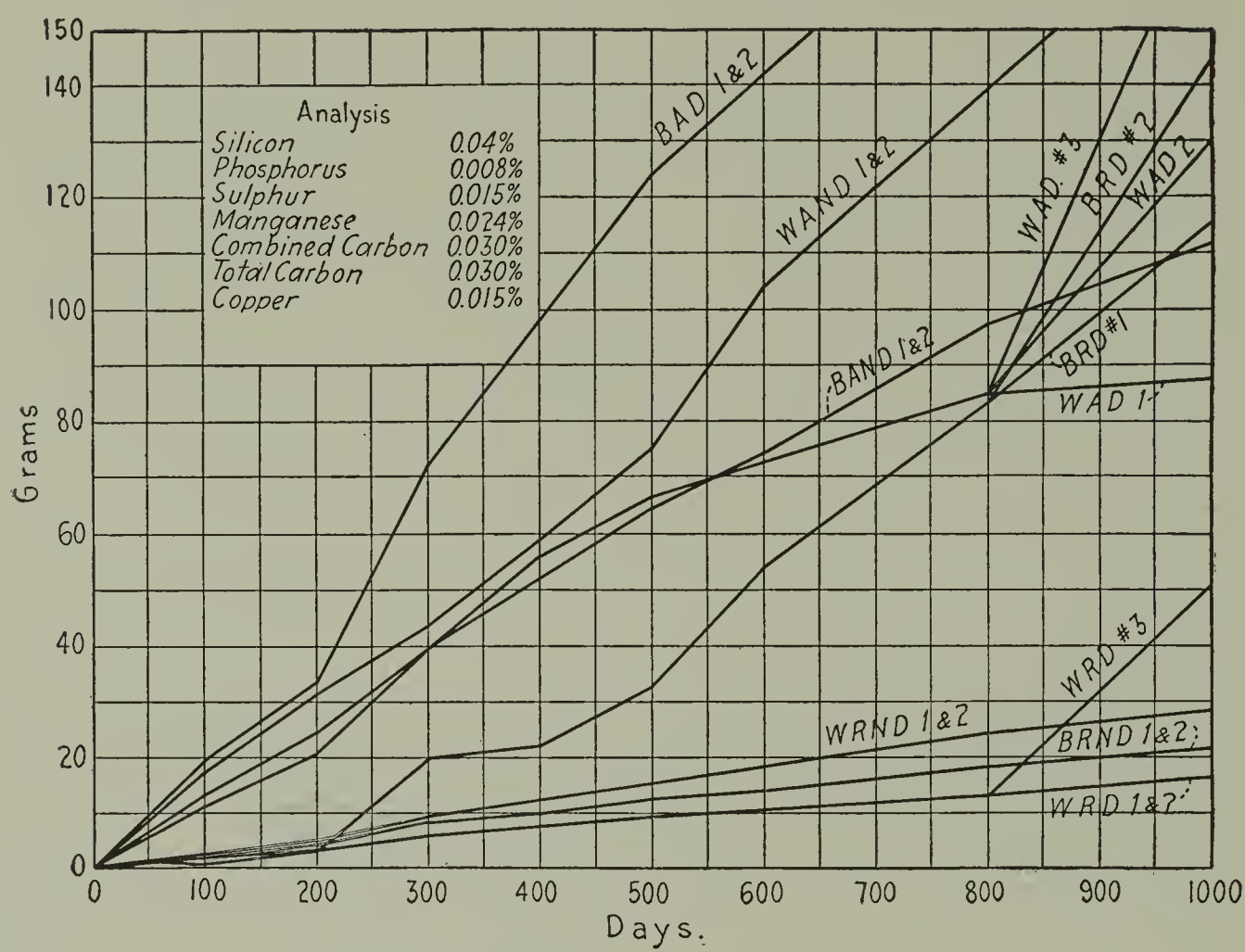

CHART 3.—BB Open Hearth Pure Iron.

All the above showed practically no pitting action.

The following are placed in order of increased pitting:

AA	CC
Least	Least
2. W. R. D.	2. W. R. D.
3. W. A. N. D.	3. W. A. N. D.
4. W. A. D.	4. W. A. D.
8. B. A. D.	8. B. A. D.
Most	Most

The pitting action in the case of 2, W. R. D., was fine and localized, the pits being better defined and deeper in the case of CC than in AA. Condition 8, B. A. D., in the case of AA showed but little pitting. The deep pitting in 3, W. A. N. D., and 4, W. A. D., was due to locally adherent mill scale. While the losses of the CC plates in these two instances did not differ very greatly from those of the AA plates, the pitting action was greater in the former than in the latter and affords an interesting illustration of the adverse influence of mill scale which is tightly adherent only locally. Uniformly adherent

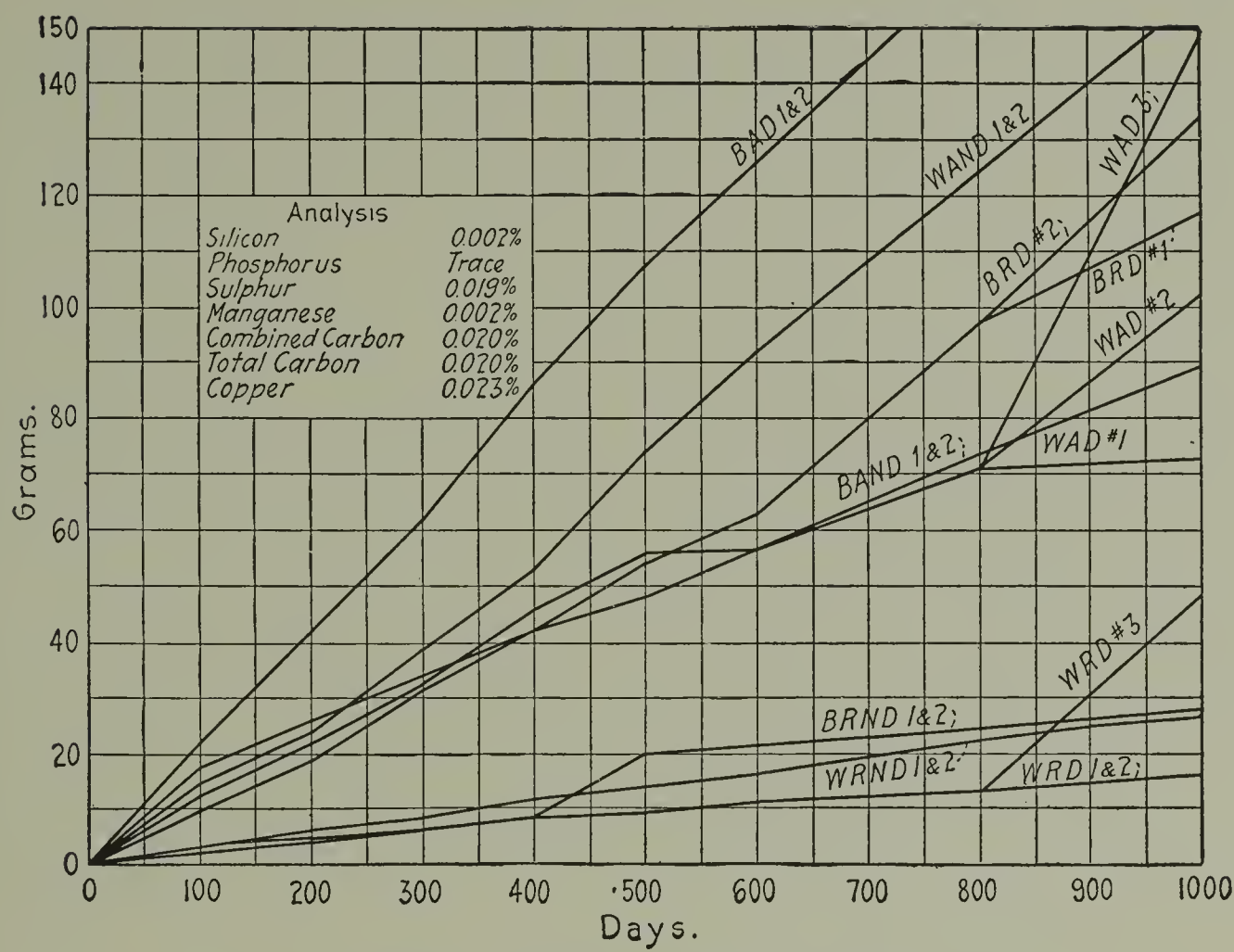

CHART 4.—II Open Hearth Pure Iron.

mill scale protects against corrosion for some time at least, but a thick coating of mill scale which resists removal during corrosion, in patches, leads to deep pitting and early failure of the metal. It seems that surface conditions rather than composition of metal caused the different behavior of the copper bearing metals, AA and CC under conditions 3, W. A. N. D., and 4, W. A. D.

OPEN-HEARTH PURE IRONS. BB AND II, BLACK FINISH; JJ AND KK, COLD ROLLED. CHARTS 3, 4, 5, AND 6

These were samples of pure iron or mild steel, whichever designation is preferred, and manufactured by the open-hearth process, which have come into prominence during the past ten years both on account of their purity and also their homogeneity and uniformity resulting from care in manufacture and in physical treatment.

The impurities as determined in these samples differed somewhat and these differences are shown in the following table:

	BB	II	JJ	KK
Impurities as determined	0.162	0.086	0.113	0.103
Iron by difference	99.84	99.91	99.89	99.90

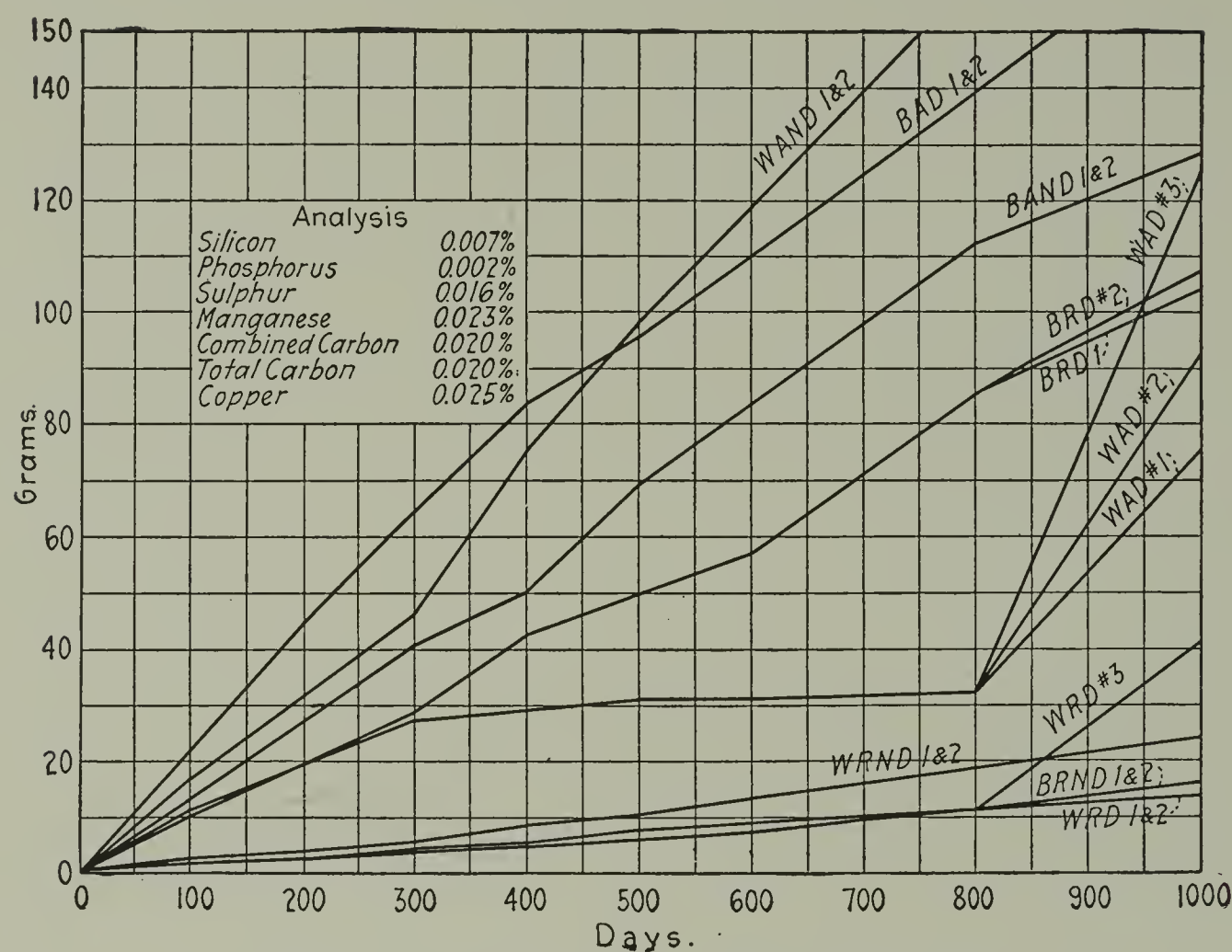

CHART 5.—JJ Open Hearth Pure Iron, Cold Rolled.

The order of corrodibility for the four samples was as follows:

BB	II	JJ	KK
Least	Least	Least	Least
5. B. R. N. D.	1. W. R. N. D.	5. B. R. N. D.	5. B. R. N. D.
1. W. R. N. D.	5. B. R. N. D.	1. W. R. N. D.	1. W. R. N. D.
2. W. R. D.	2. W. R. D.	2. W. R. D.	2. W. R. D.
7. B. A. N. D.	7. B. A. N. D.	6. B. R. D.	7. B. A. N. D.
6. B. R. D.	6. B. R. D.	4. W. A. D.	6. B. R. D.
4. W. A. D.	4. W. A. D.	7. B. A. N. D.	4. W. A. D.
3. W. A. N. D.	3. W. A. N. D.	8. B. A. D.	3. W. A. N. D.
8. B. A. D.	8. B. A. D.	3. W. A. N. D.	8. B. A. D.
Most	Most	Most	Most

From the charts it will be seen that the three conditions, 5, B. R. N. D., 1, W. R. N. D., and 2, W. R. D., none of which included agitation by air, group themselves together and show the smallest amount of corrosion. Condition 2, W. R. D., in all cases develops a layer of magnetic oxide which when removed by sand blasting produces the greatest loss in weight of the three conditions. Con-

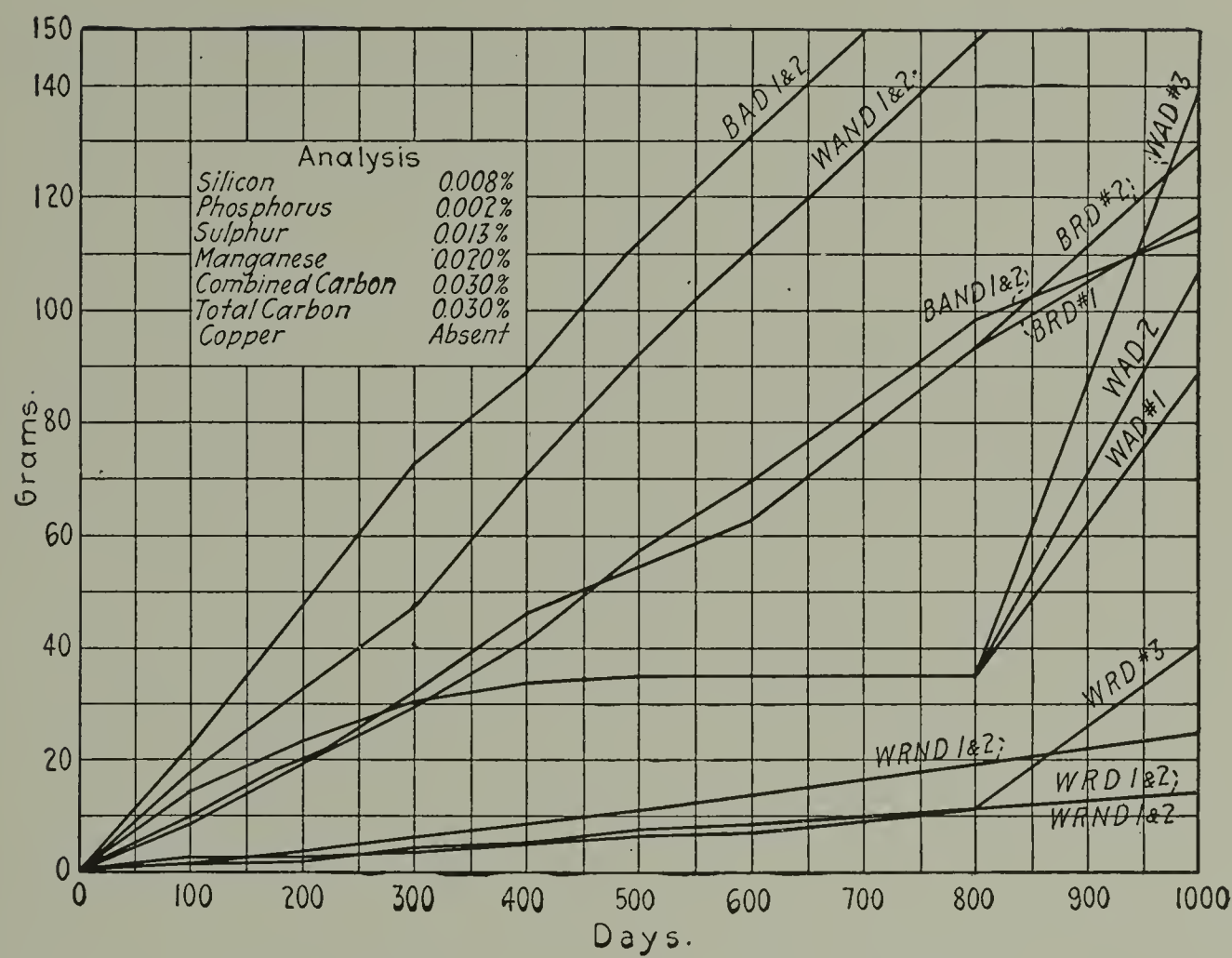

CHART 6.—KK Open Hearth Pure Iron, Cold Rolled.

ditions 7, B. A. N. D., 6, B. R. D., 3, W. A. N. D., 4, W. A. D., and 8, B. A. D. also group themselves together and among these the one with anomalous behavior is 4, W. A. D., which develops a protective coating of adherent rust and while not losing as much weight as it should during the course of the experiment, when cleaned by sand blasting discloses the fact that considerable corrosion has taken place. All of the plates under these five conditions were subjected to the influence of air with the exception of those under condition 6, B. R. D., which nevertheless takes its place with those showing the greater amount of corrosion.

Those showing the greatest amount of pitting in all cases were as follows: Conditions 2, W. R. D., 3, W. A. N. D., 4, W. A. D., and 8, B. A. D. Condition 8, B. A. D., produced not only deep pitting, but also general corrosion to such an extent that very little was left of the plates at the close of the experiment, 1000 days. In all other cases there was no pitting action, the corrosion taking place rather uniformly over the entire surface.

An inspection of Charts 3, 4, 5 and 6 indicates that the course of corrosion in the case of these pure open-hearth irons does not differ

essentially from that of the copper bearing metals, AA and CC, or the ordinary open-hearth irons, UU and WW, and Bessemer irons, TT and VV (see below). The curves in the case of the copper-bearing metals and also the pure irons are as a rule somewhat more regular however than in Charts 7, 8, 9 and 10, ordinary open-hearth and Bessemer irons, but it is difficult to judge how important this point is. Judging by the appearance of the plates, which, under the same conditions was similar, under conditions 4, W. A. D., sample WW, ordinary open-hearth iron, and VV, ordinary Bessemer, suffered more and failed earlier than did the others. On the other hand, UU, ordinary open hearth, and TT, Bessemer, resisted corrosion as well as any of the rolled metals.

Open Hearth Irons, UU and WW. Charts 7 and 8

The order of corrosion was as follows:

UU	WW
Least	Least
5. B. R. N. D.	5. B. R. N. D.
1. W. R. N. D.	1. W. R. N. D.
2. W. R. D.	2. W. R. D.
7. B. A. N. D.	7. B. A. N. D.
4. W. A. D.	6. B. R. D.
6. B. R. D.	4. W. A. D.
3. W. A. N. D.	8. B. A. D.
8. B. A. D.	3. W. A. N. D.
Most	Most

The curves group themselves in general as in the case of the copper-bearing metals and the open-hearth pure irons, Conditions 5, B. R. N. D., 1, W. R. N. D., and 2, W. R. D., showing the least corrosion and the other five conditions showing the most. Conditions 2, W. R. D., and 4, W. A. D., show their usual erratic behavior due to the tightly adhering layer of rust formed, this phenomenon being pronounced in the case of UU and much less so in the case of WW. Under condition 8, B. A. D., sample UU showed little tendency to form an adherent layer of rust whereas sample WW was apparently to some extent protected in this manner. This is only disclosed in the curve by the change in direction after 400 days since the plates were too thin at the last for sand blasting.

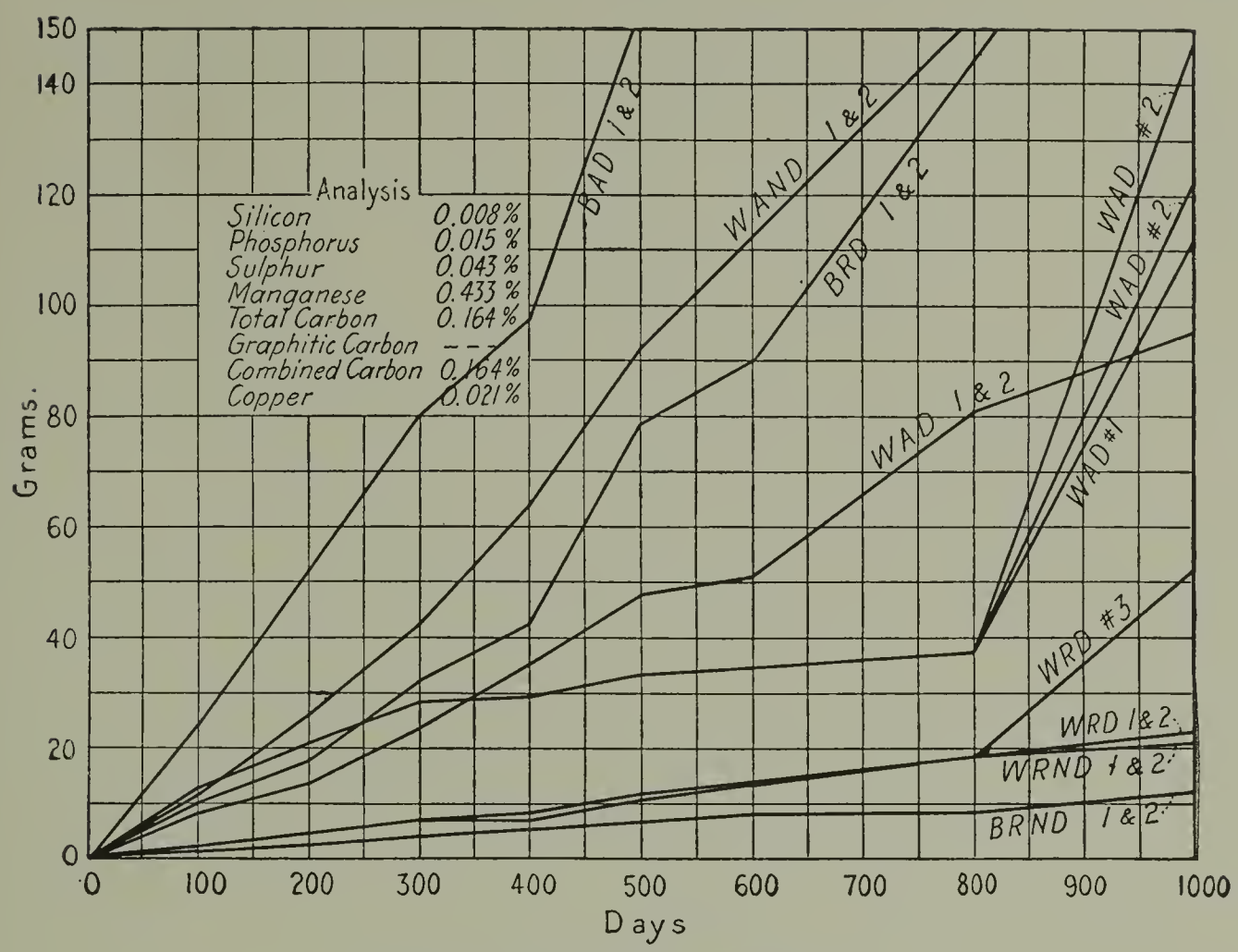

CHART 7.—UU Open Hearth Iron.

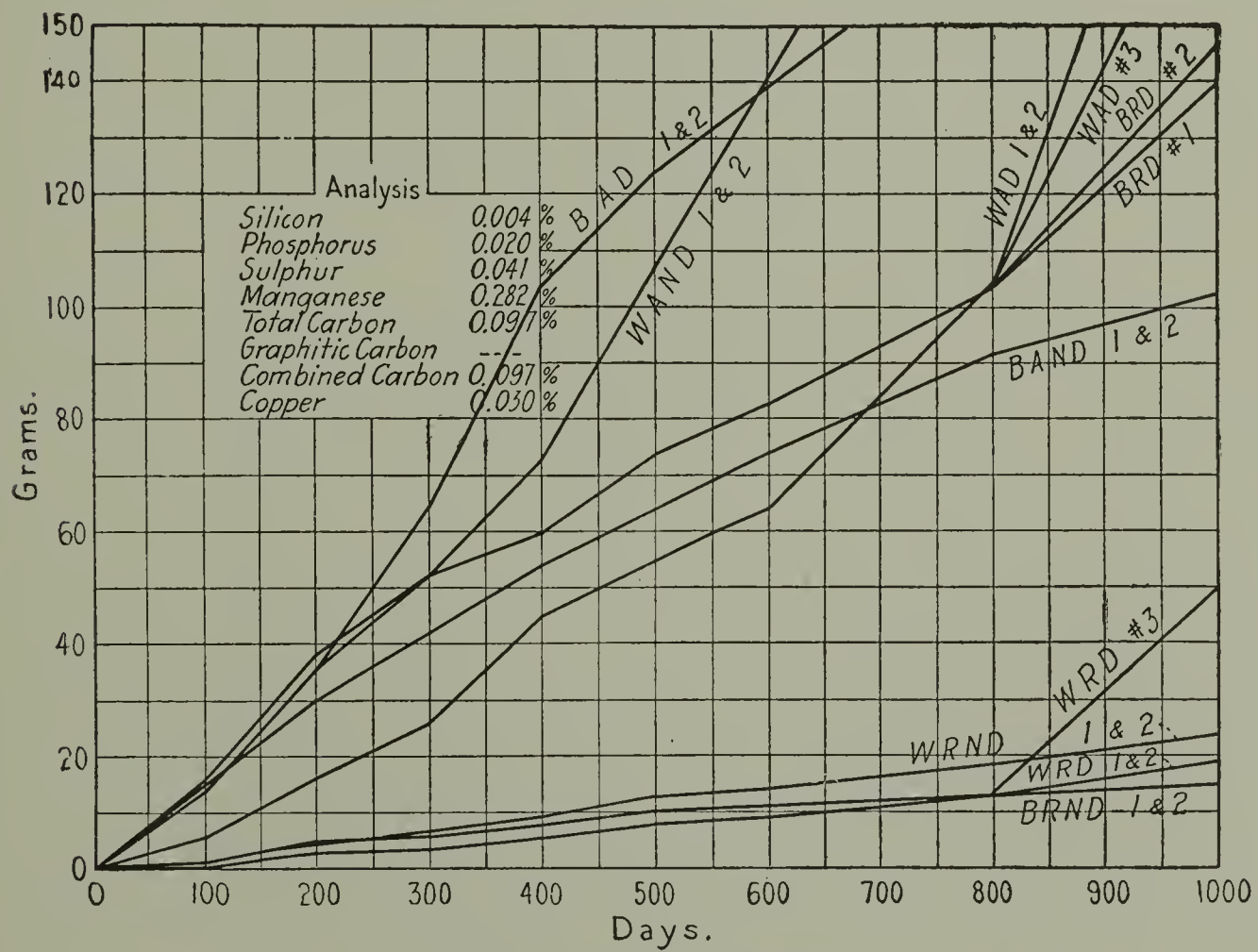

CHART 8.—WW Open Hearth Iron.

Bessemer Irons. TT and VV. Charts 9 and 10

The order of corrosion was as follows:

TT	VV
Least	Least
5. B. R. N. D.	5. B. R. N. D.
1. W. R. N. D.	1. W. R. N. D.
2. W. R. D.	2. W. R. D.
7. B. A. N. D.	7. B. A. N. D.
4. W. A. D.	6. B. R. D.
6. B. R. D.	4. W. A. D.
3. W. A. N. D.	8. B. A. D.
8. B. A. D.	3. W. A. N. D.
Most	Most

The curves group themselves as in the previous examples, but there appears to be more irregularity in the group of five, which show corrodibility. The irregularities shown in the group of five are probably due to the falling off of rust at irregular periods. The third weight on sample VV, condition 4, W. A. D., is wanting because at the end of the experiments the plates were practically corroded away and the fragments remaining could not be sand blasted. If a final weight could have been taken after sand blasting in this case, undoubtedly the curve after 800 days would have followed as steep an ascent or steeper than that in the case of sample TT. A hypothetical line marked W. A. D. 3 has been drawn into the chart to call attention to this point.

Puddled Irons, DD and EE. Charts 11 and 12

The order of corrosion in the case of these two samples was as follows:

DD	EE
Least	Least
5. B. R. N. D.	5. B. R. N. D.
1. W. R. N. D.	1. W. R. N. D.
2. W. R. D.	2. W. R. D.
7. B. A. N. D.	4. W. A. D.
4. W. A. D.	6. B. R. D.
6. B. R. D.	7. B. A. N. D.
3. W. A. N. D.	8. B. A. D.
8. B. A. D.	3. W. A. N. D.
Most	Most

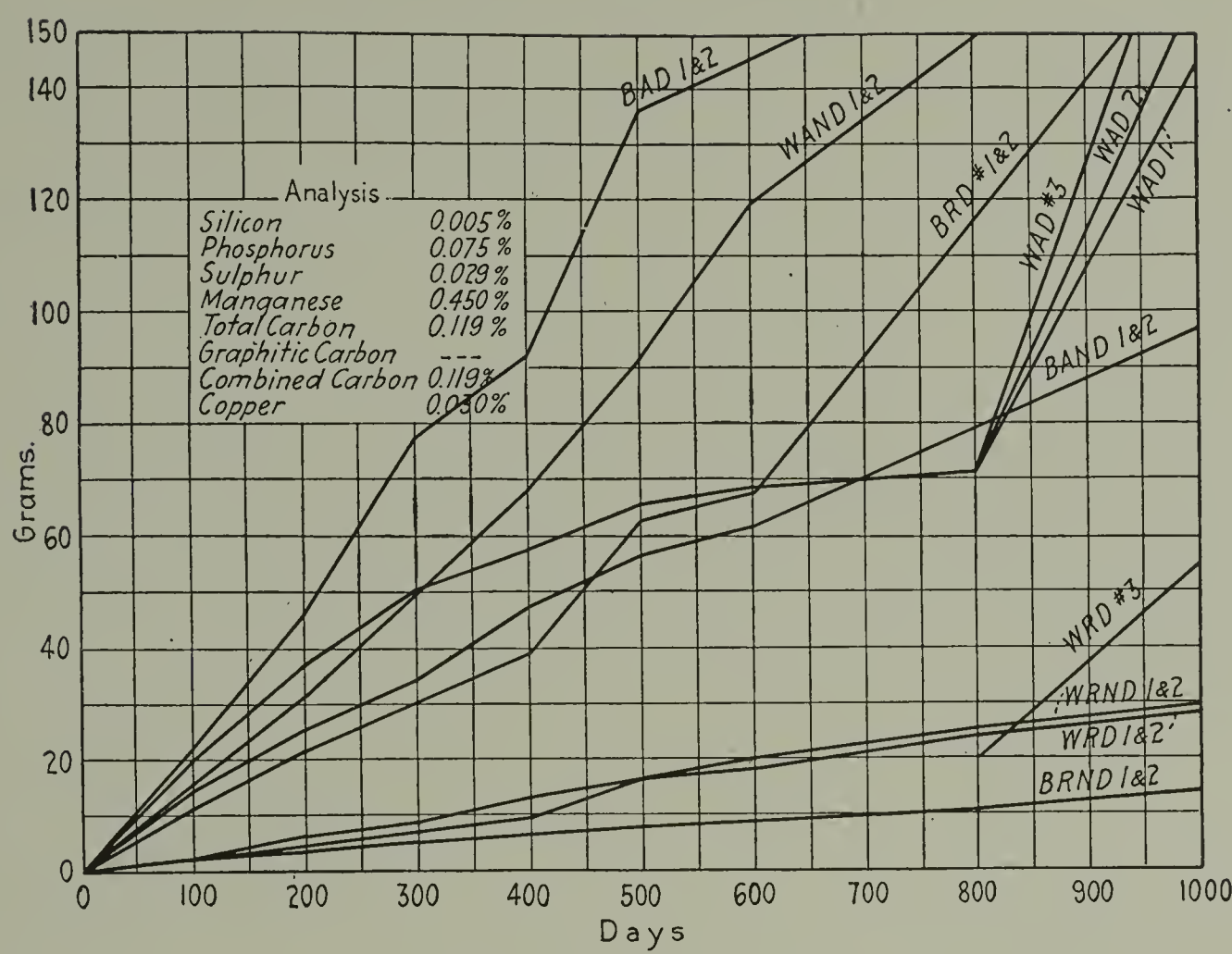

CHART 9.—TT Bessemer Iron.

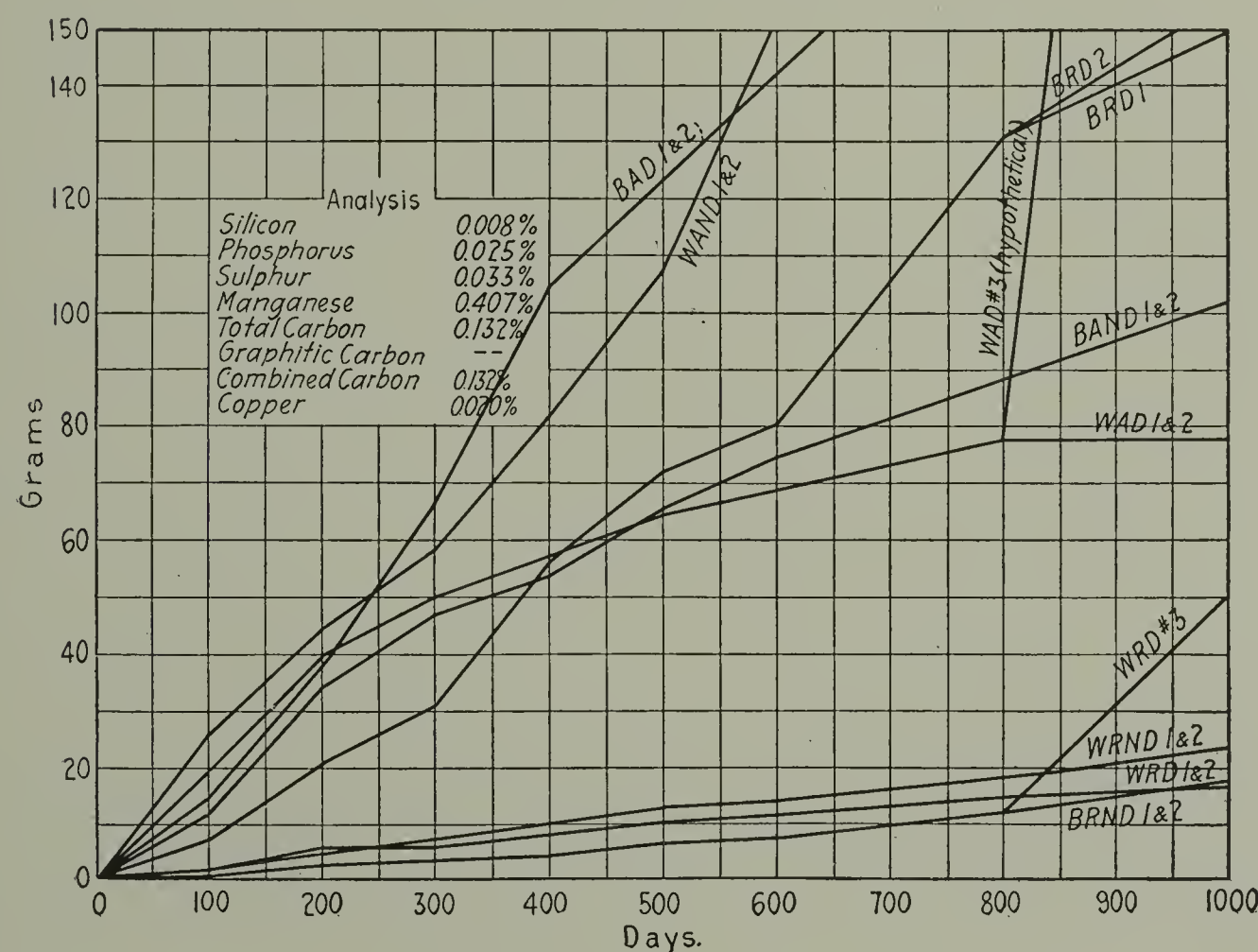

CHART 10.—VV Bessemer Iron.

The curves for samples DD and EE are different from those previously considered and also are quite different in respect to each other. The composition of the two metals is somewhat different, particularly as regards manganese, DD containing .31 per cent of this element and EE .03 per cent. In structure DD bears more resemblance to an ordinary rolled metal whereas EE shows more of the fibrous structure characteristic of some puddled irons. The characteristic grouping of the previously considered curves is not apparent in these, the chart for DD showing rather uniformly distributed lines and that of EE a lower group of five and an upper group of three. Rust shows a greater tendency to adhere in these metals than in those previously considered. In regard to pitting action the following order prevailed:

DD	EE
Least	Least
2. W . R. D.	2. W. R. D.
6. B. R. D.	6. B. R. D.
4. W. A. D.	4. W. A. D.
3. W. A. N. D.	3. W. A. N. D.
8. B. A. D.	8. B. A. D.
Most	Most

The order of pitting action in the case of 3, W. A. N. D., and 4, W. A. D., was undoubtedly due to the adherence of mill scale in the case of 3, W. A. N. D., so that these samples showed deeper pitting and more perforations than 4, W. A. D.

Charcoal Iron, XX. Chart 13

Only one sample of charcoal iron could be obtained at the time the experiments were started. This iron corroded more rapidly than any of the other samples and so many of the plates had corroded away or were rapidly disappearing at 500 days that the experiment was discontinued. This period was, however, long enough to demonstrate the direction of the curves. The order of corrosion was as follows:

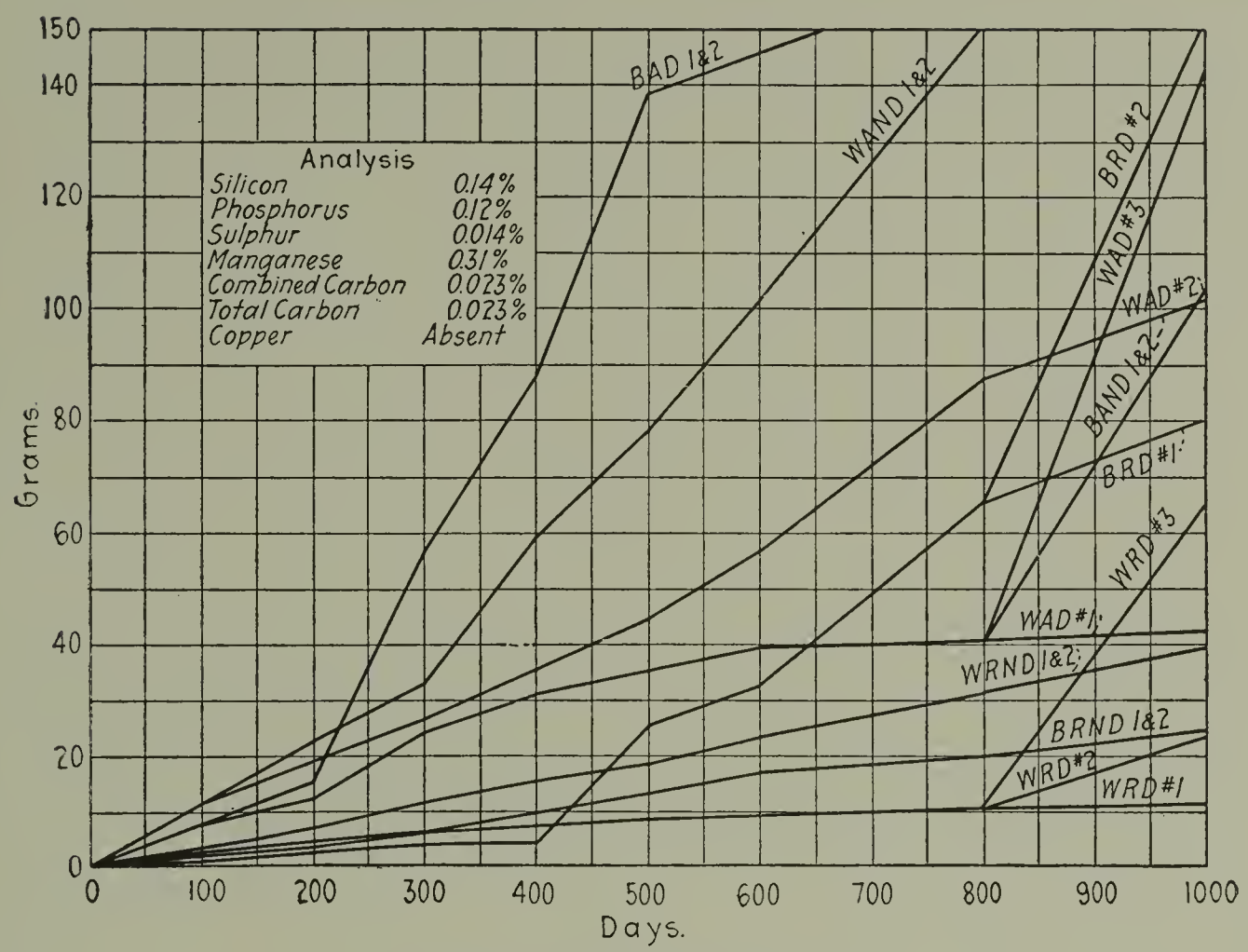

CHART 11.—DD Puddled Iron.

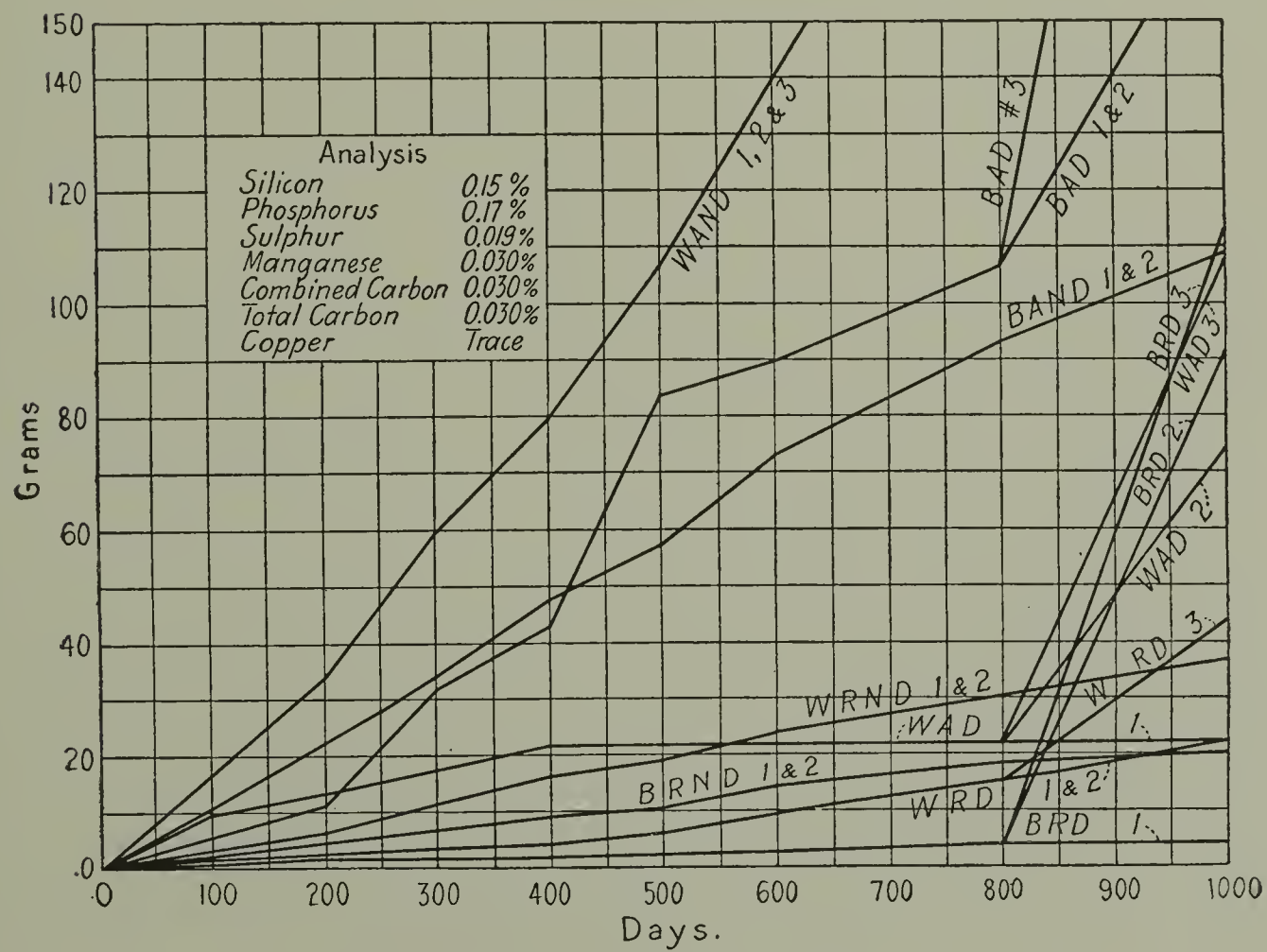

CHART 12.—EE Puddled Iron.

XX

Least

5. B. R. N. D.
1. W. R. N. D.
2. W. R. D.
7. B A. N. D.
6 B. R. D.
8. B. A. D.
4. W. A D.
3. W. A. N. D.

Most

The curves group themselves into a lower group of three consisting of 5, B. R. N. D., 1, W. R. N. D., and 2, W. R. D., a middle group of two consisting of 7, B. A. N. D., and 6, B. R. D., and an upper group of three consisting of 8, B. A. D., 4, W. A. D., and 3, W. A. N. D.

The order of pitting was as follows:

Least

6. B. R. D.
2. W. R. D.
3. W. A. N. D.
8. B. A. D.
4. W. A. D.

Most

Both under the conditions which caused pitting and under other conditions charcoal iron suffered more than any iron in the series.

Gray Cast Irons, FF and SS. Charts 14 and 15

The curves of the cast metals show at a glance a lower amount of corrosion in the majority of cases and a greater tendency for the products of corrosion to adhere closely than do the rolled metals. In a few cases, particularly MM, white iron, LL, malleable iron, NN, malleable iron, PP, cast steel and QQ cast steel, the W. A. N. D. curves are similar to those of the rolled metals and the B. A. D. curve for FF, cast steel, bears some resemblance to that of the puddled irons. For the rest, the general appearance of the charts is different from those representing the rolled plates.

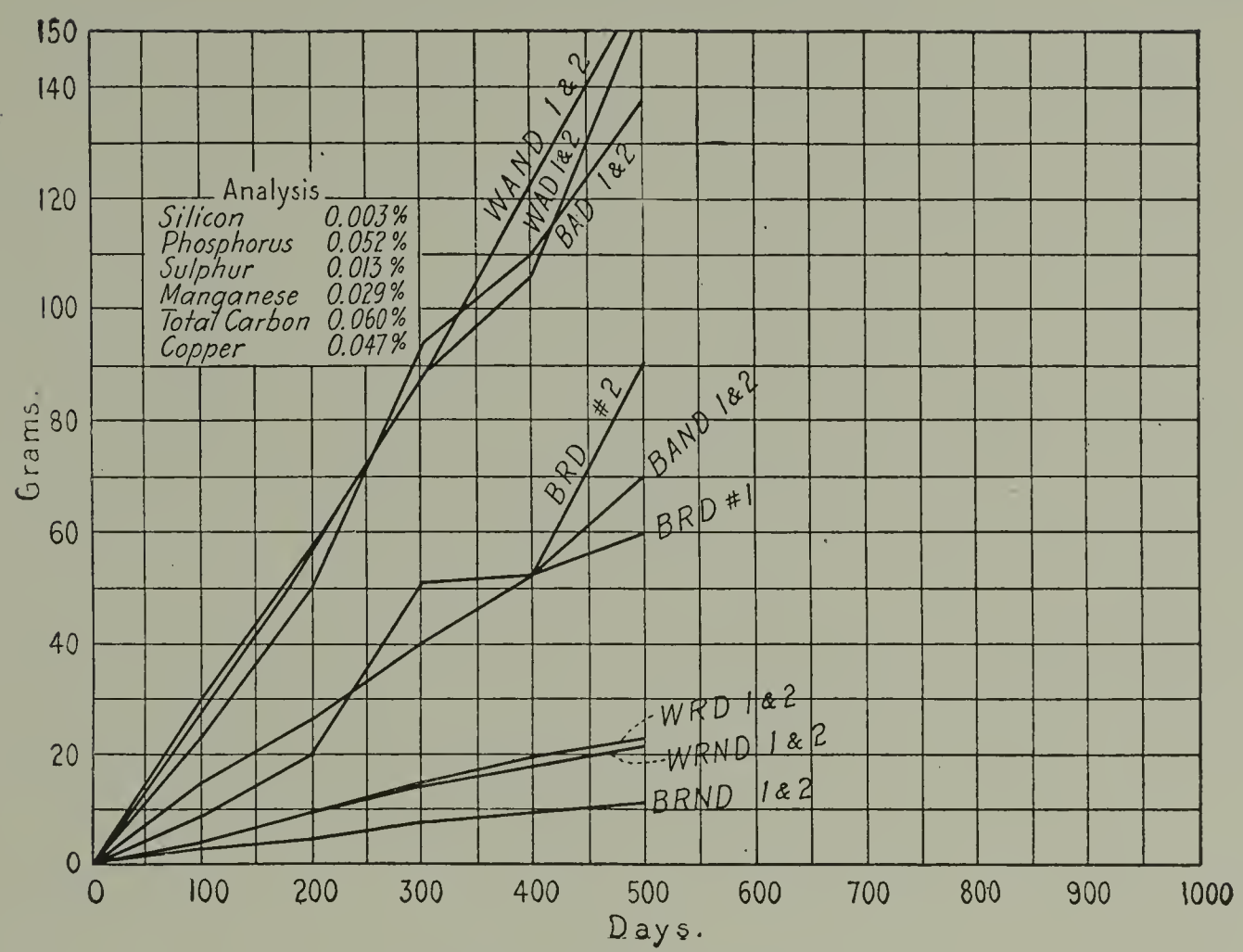

CHART 13.—XX Charcoal Iron.

The order of corrodibility for the gray cast irons was as follows:

FF	SS
Least	Least
5. B. R. N. D.	5. B. R. N. D.
2. W. R. D.	1. W. R. N. D.
1. W. R. N. D.	2. W. R. D.
4. W. A. D.	4. W. A. D.
3. W. A. N. D.	6. B. R. D.
7. B. A. N. D.	3. W. A. N. D.
6. B. R. D.	7. B. A. N. D.
8. B. A. D.	8. B. A. D.
Most	Most

The curves arrange themselves into a lower group of five consisting of 2, W. R. D., 4, W. A. D., 5, B. R. N. D., 1, W. R. N. D. and 6, B. R. D., and an upper group of three consisting of 3, W. A. N.D 7, B. A. N. D., and 8, B. A. D.

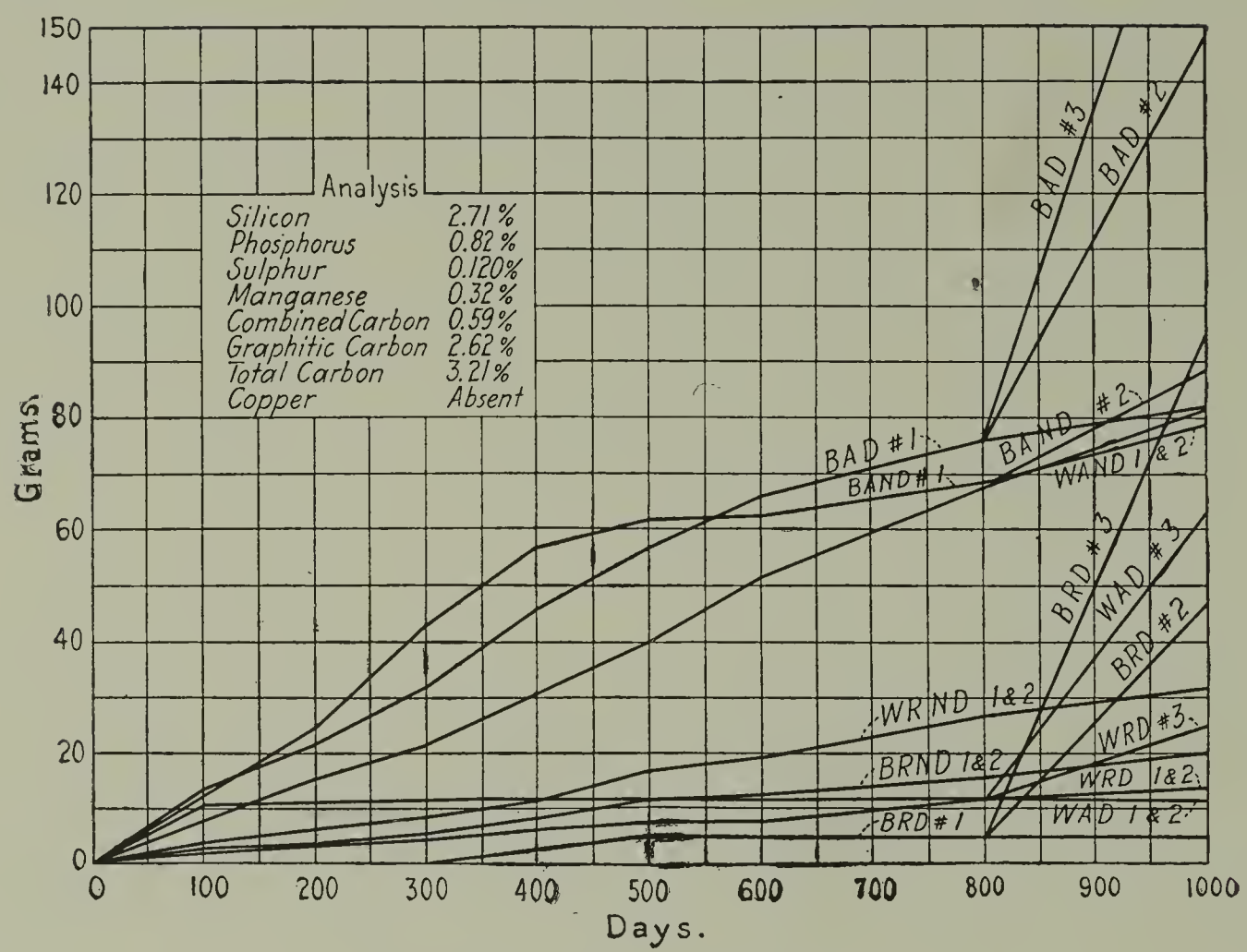

CHART 14.—FF Gray Cast Iron.

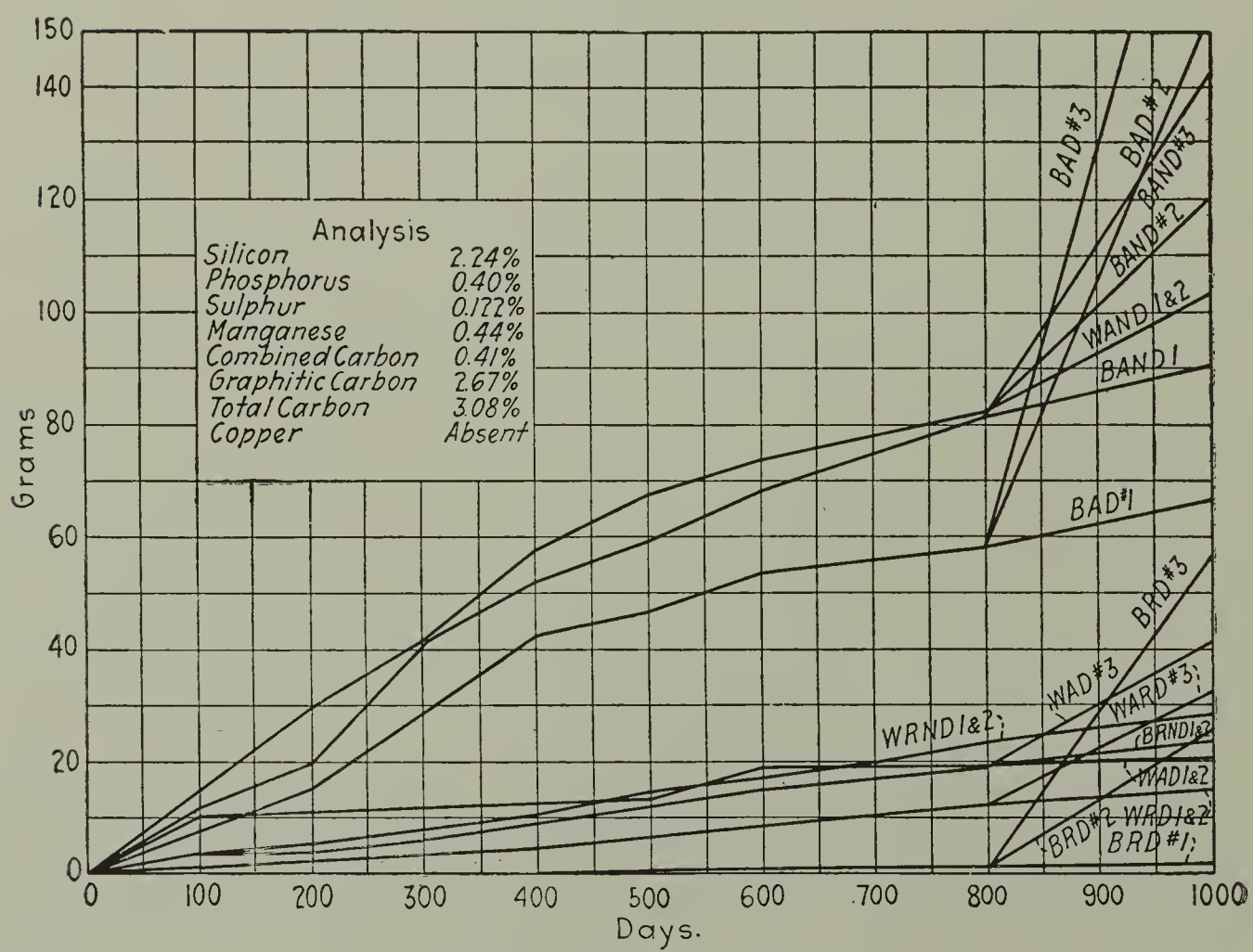

CHART 15.—SS Gray Cast Iron.

When one considers the small amount of corrosion which occurs in the case of gray cast iron compared with that which occurs in the case of the much purer rolled metals and particularly the pure open-hearth iron, an investigator may be forgiven for becoming a skeptic on the subject of the electrolytic theory of corrosion as it has sometimes been presented in the past. An addition to the theory is required to explain why gray cast iron with its considerable percentage of impurities should corrode rather less than other and purer metals. That adherent rust protects it to a considerable extent can scarcely be doubted, but that this is the only protective influence it would be unsafe to say at present. Cast iron corrodes with a fair degree of rapidity under several conditions, but a glance at the curves, which are very similar for both FF and SS, reveals a strong tendency for the upper group of three to bend toward the horizontal due to the adherence of rust which when removed gives them a sharp turn upward.

The order of pitting was as follows:

FF	SS
Least	Least
2. W. R. D. (none)	2. W. R. D. (none)
4. W. A. D.	4. W. A. D.
6. B. R. D.	6. B. R. D.
7. B. A. N. D.	7. B. A. N. D.
8. B. A. D.	8. B. A. D.
Most	Most

The above order, it will be noticed, is different from that of the majority of the rolled plates. In particular, 3, W. A. N. D. and 4, W. A. D. show less pitting than any of the rolled metals. Perforations occurred under condition 8, B. A. D.

White Cast Irons, LL and OO. Charts 16 and 17

The two samples referred to under this designation were purchased from two different manufacturers although the analyses run fairly close together. Sample LL contains 1.35 per cent total carbon

and sample OO 1.55. The silicon contents are .81 and .48 respectively. Nevertheless, the curves of the two samples are somewhat different, particularly the W. A. N. D. curves, owing to the closer adherence of rust to sample OO than to sample LL. It is difficult to see on the basis of composition why rust should adhere more closely in one case than in the other. Is it possible that the slightly higher carbon in sample OO caused the difference?

The order of corrodibility for the two samples was as follows:

LL	OO
Least	Least
2. W. R. D.	5. B. R. N. D.
5. B. R. N. D.	2. W. R. D.
1. W. R. N. D.	1. W. R. N. D.
4. W. A. D.	4. W. A. D.
6. B. R. D.	6. B. R. D.
7. B. A. N. D.	7. B. A. N. D.
8. B. A. D.	3. W. A. N. D.
3. W. A. N. D.	8. B. A. D.
Most	Most

The order of pitting was as follows:

LL	OO
Least	Least
2. W. R. D.	2. W. R. D. (slight)
4. W. A. D.	3. W. A. N. D.
3. W. A. N. D.	4. W. A. D.
6. B. R. D.	6. B. R. D.
8. B. A. D.	8. B. A. D.
Most	Most

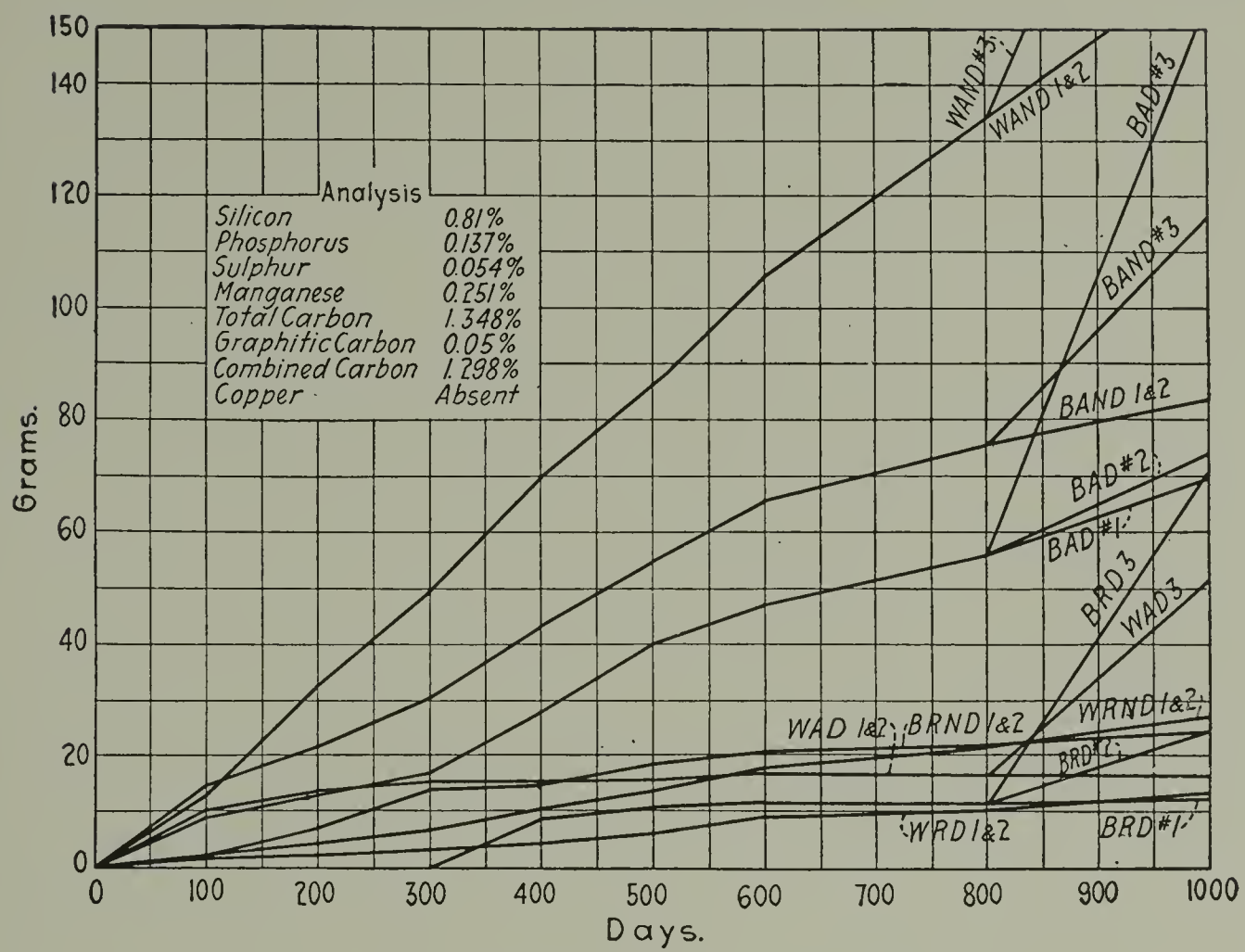

CHART 16.—LL White Cast Iron.

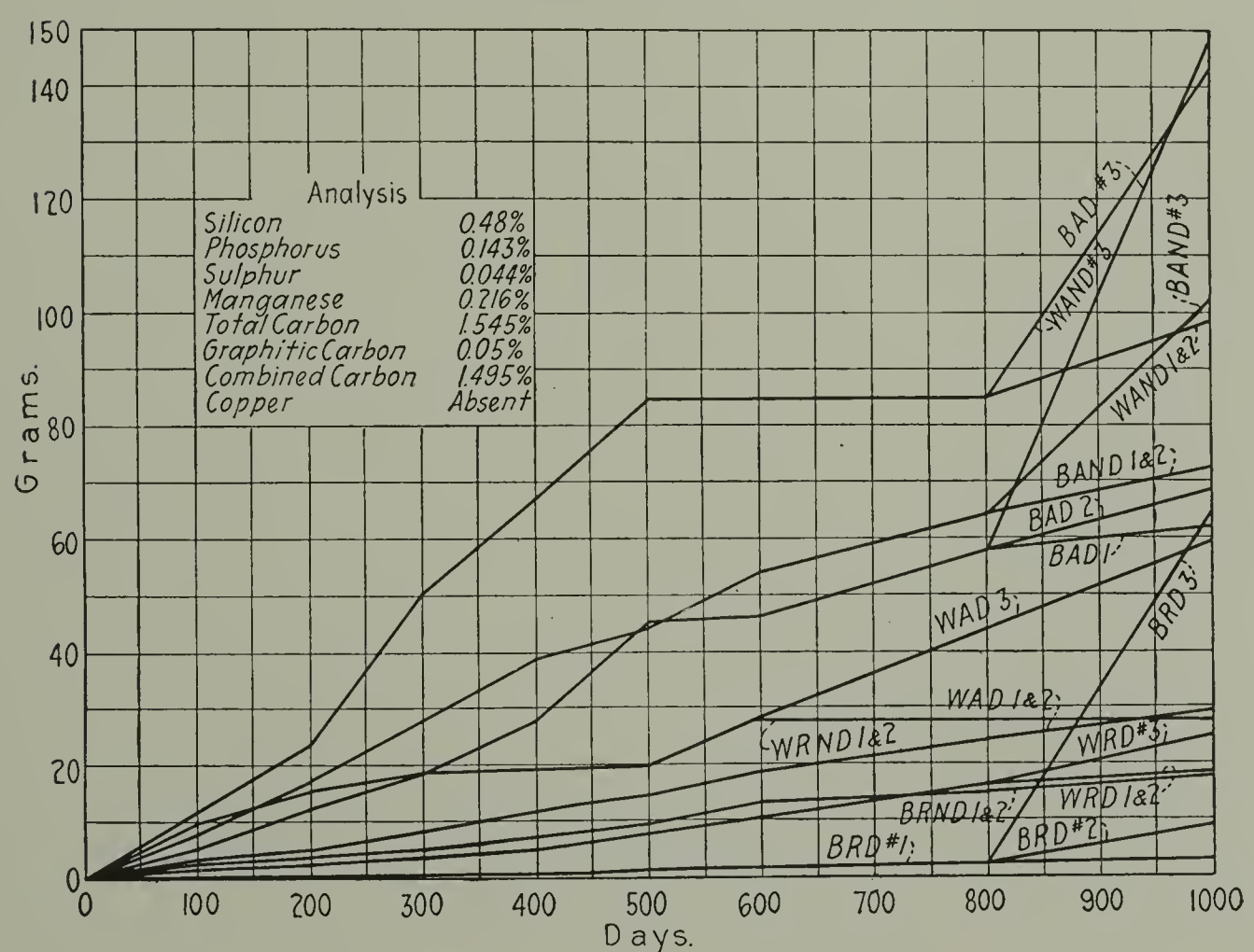

CHART 17.—DD White Cast Iron.

Malleable Irons, MM and NN. Charts 18 and 19

These two samples differ considerably in composition particularly as regards carbon content. They were bought from two different foundries, by name, and without definite specifications. Nevertheless the curves for both samples are very similar. In particular the curves for conditions 3, W. A. N. D. and 7, B. A. N. D. return to their old form as in the rolled metals. There did not appear to be any greater rust adhesion in one sample than in the other.

The following was the order of corrosion:

MM	NN
Least	Least
5. B. R. N. D.	5. B. R. N. D.
1. W. R. N. D.	1. W. R. N. D.
2. W. R. D.	2. W. R. D.
4. W. A. D.	4. W. A. D.
6. B. R. D.	6. B. R. D.
7. B. A. N. D.	7. B. A. N. D.
8. B. A. D.	8. B. A. D.
3. W. A. N. D.	3. W. A. N. D.
Most	Most

The order of pitting was as follows:

MM	NN
2. W. R. D.	2. W. R. D.
7. B. A. N. D.	7. B. A. N. D.
3. W. A. N. D.	4. W. A. D.
4. W. A. D.	3. W. A. N. D.
6. B. R. D.	6. B. R. D.
8. B. A. D.	8. B. A. D.
Most	Most

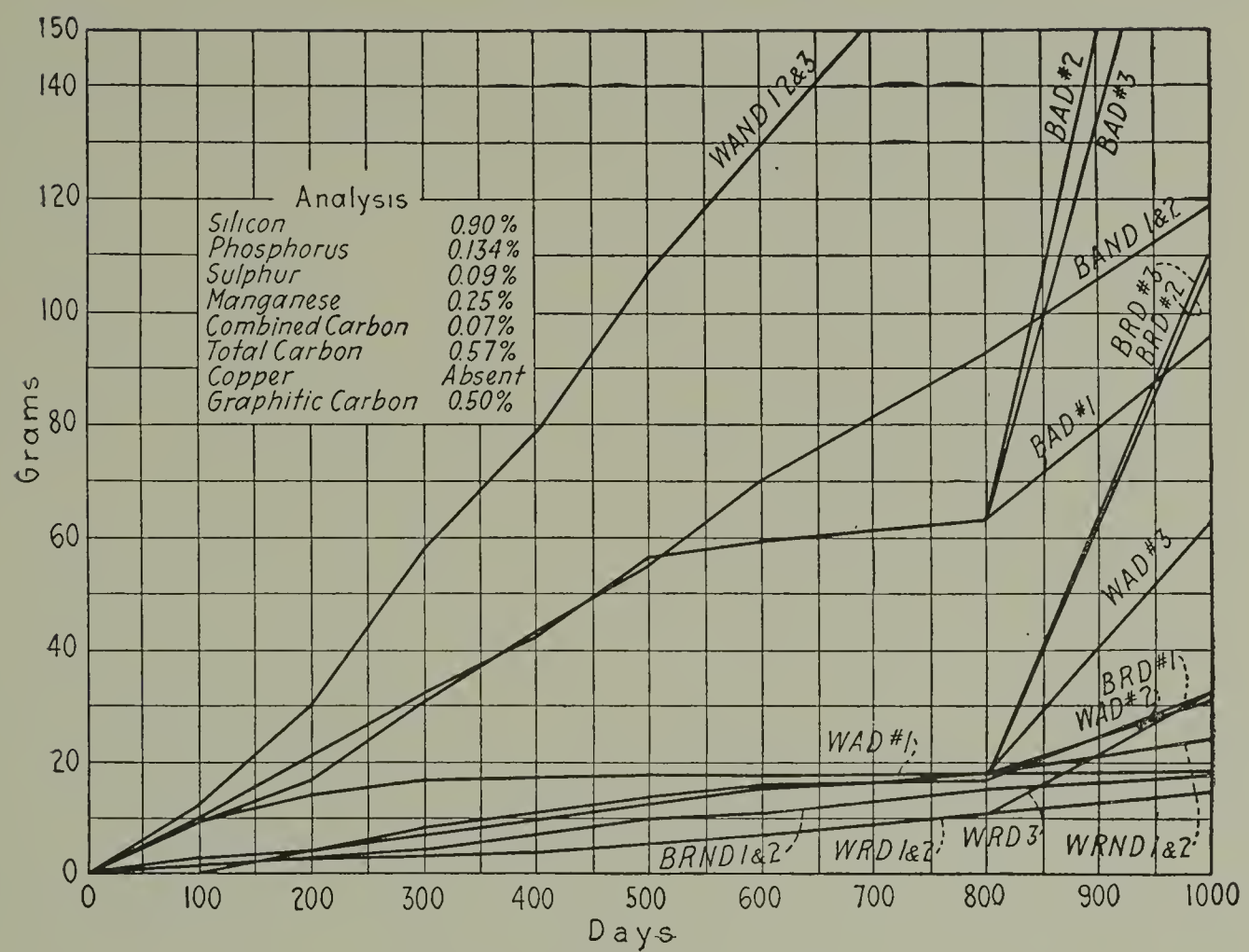

CHART 18.—MM Malleable Iron.

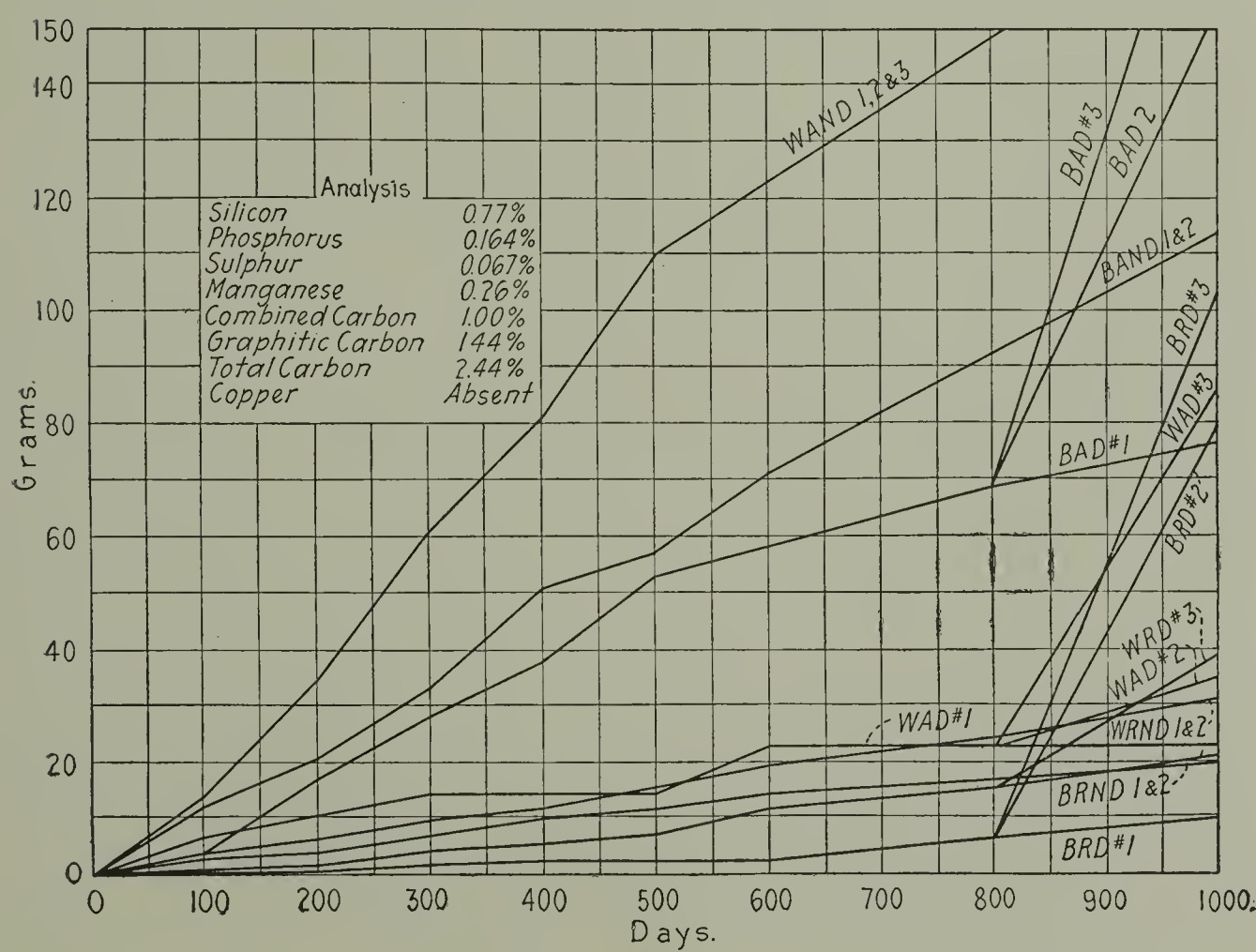

CHART 19.—NN Malleable Iron.

Semi Steels, GG and RR. Charts 20 and 21

The order of corrosion was as follows:

GG	RR
Least	Least
5. B. R. N. D.	5. B. R. N. D.
2. W. R. D.	2. W. R. D.
1. W. R. N. D.	1. W. R. N. D.
4. W. A. D.	4. W. A. D.
6. B. R. D.	6. B. R. D.
3. W. A. N. D.	3. W. A. N. D.
7. B. A. N. D.	6. B. A. N. D.
8. B. A. D.	8. B. A. D.
Most	Most

The curves for the two samples of semi-steel, which are very similar, bear a close resemblance to those representing the two samples of gray cast iron, FF and SS, as they should from their nature and composition. The curves are arranged in a lower group of five and an upper group of three, the latter consisting of 8, B. A. D., 7, B. A. N. D. 7, B. A. N. D., and 3, W. A. N. D., as in the case of the cast-iron samples.

The order of pitting was as follows:

GG	RR
Least	Least
2. W. R. D. (practically none)	2. W. R. D. (practically none)
4. W. A. D.	4. W. A. D.
7. B. A. N. D.	7. B. A. N. D.
6. B. R. D.	6. B. R. D.
8. B. A. D.	8. B. A. D.
Most	Most

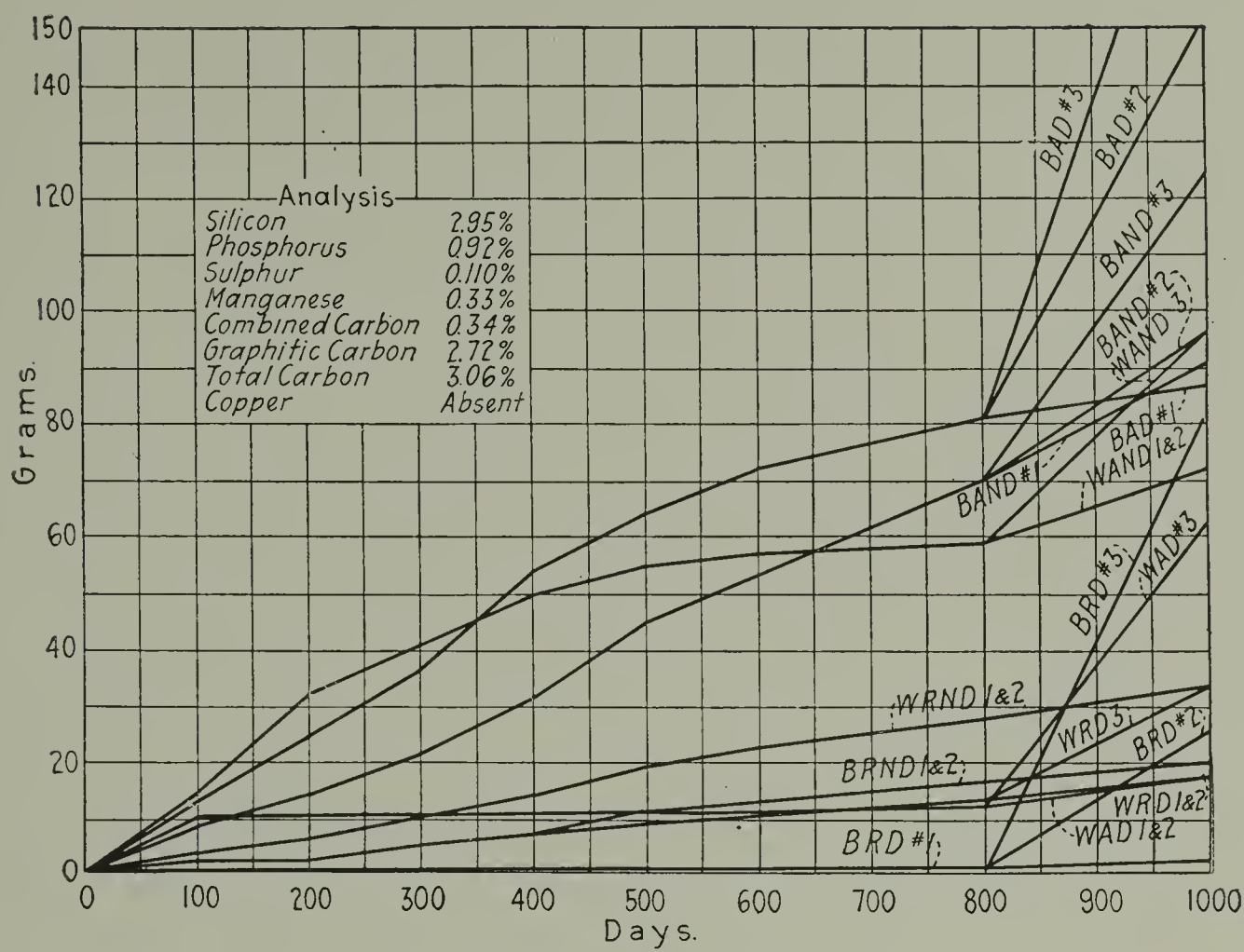

CHART 20.—GG Semi-steel.

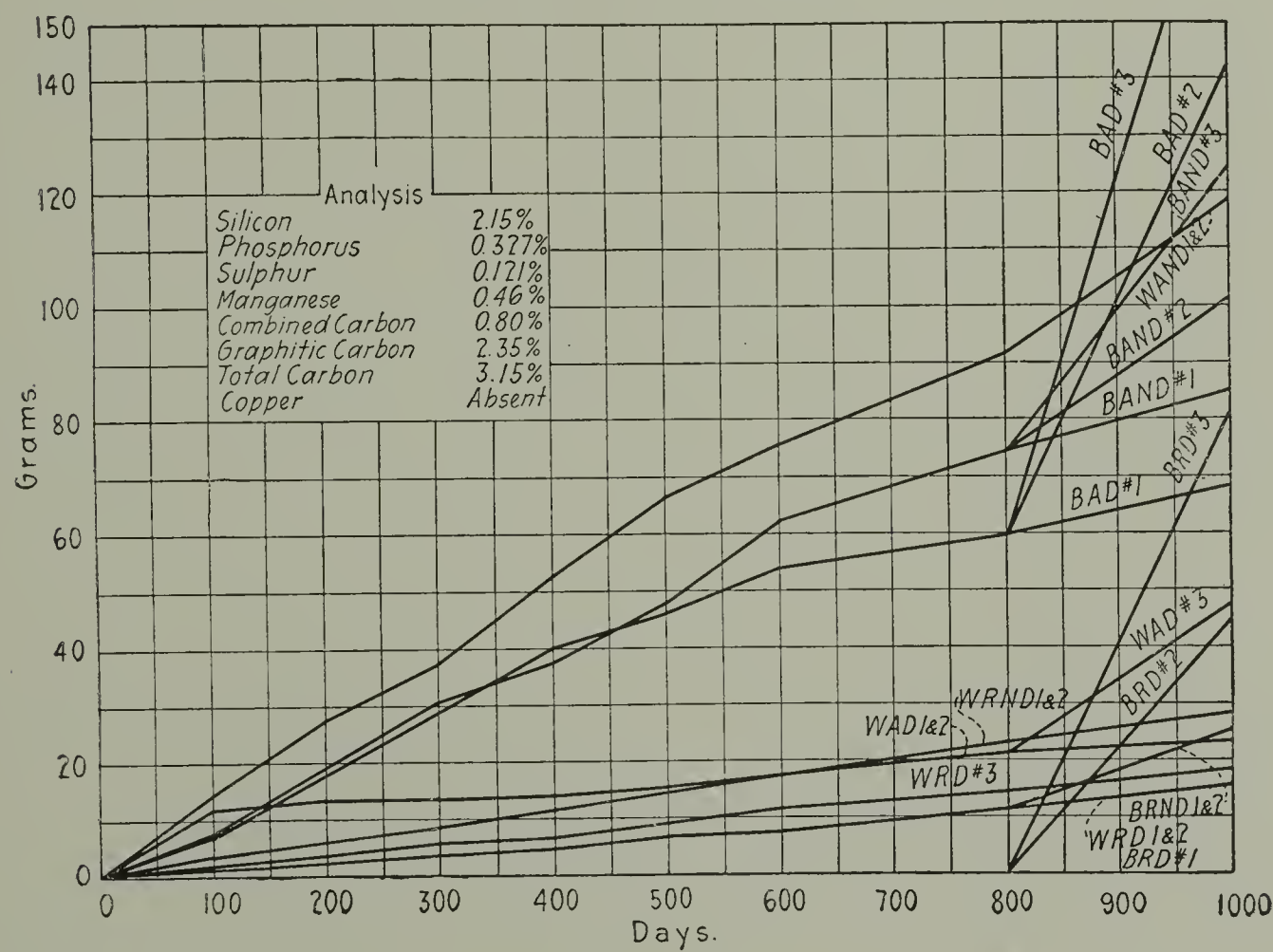

CHART 21.—RR Semi-steel.

Cast Steels, PP and QQ. Charts 22 and 23

The two samples of cast steel were very similar in their content of the elements manganese and carbon but differed in their content of phosphorus and sulphur, QQ containing more of these elements than PP.

The following was the order of corrosion:

PP	QQ
Least	Least
5. B. R. N. D.	5. B. R. N. D.
1. W. R. N. D.	1. W. R. N. D.
2. W. R. D.	2. W. R. D.
7. B. A. N. D	7. B. A. N. D.
4. W. A. D.	4. W. A. D.
6. B. R. D.	6. B. R. D.
3. W. A. N. D.	8. B. A. D.
8. B. A. D.	3. W. A. N. D.
Most	Most

The W. A. N. D. curves of both metals are similar to those of the rolled metals and to a lesser extent the B. A. N. D. curve is also. The B. A. D. curve shows several sharp breaks due to the formation and scaling off of rust. Perhaps the most interesting feature of these plates was the amount of magnetic oxide formed under condition 2, W. R. D. which shows in the curve in the form of a rapid ascent after 800 days since these plates were sand blasted at the end of the 1000 days' period. Under conditions 6, B. R. D., and 8, B. A. D., the plates were severely pitted and perforated, the action being more intense in the case of PP than in QQ. All of the plates under conditions promoting pitting were badly pitted and perforated, the order being as follows:

PP	QQ
Least	Least
2. W. R. D.	2. W. R. D.
3. W. A. N. D.	3. W. A. N. D.
4. W. A. D.	4. W. A. D.
6. B. R. D.	6. B. R. D.
8. B. A. D.	8. B. A. D.
Most	Most

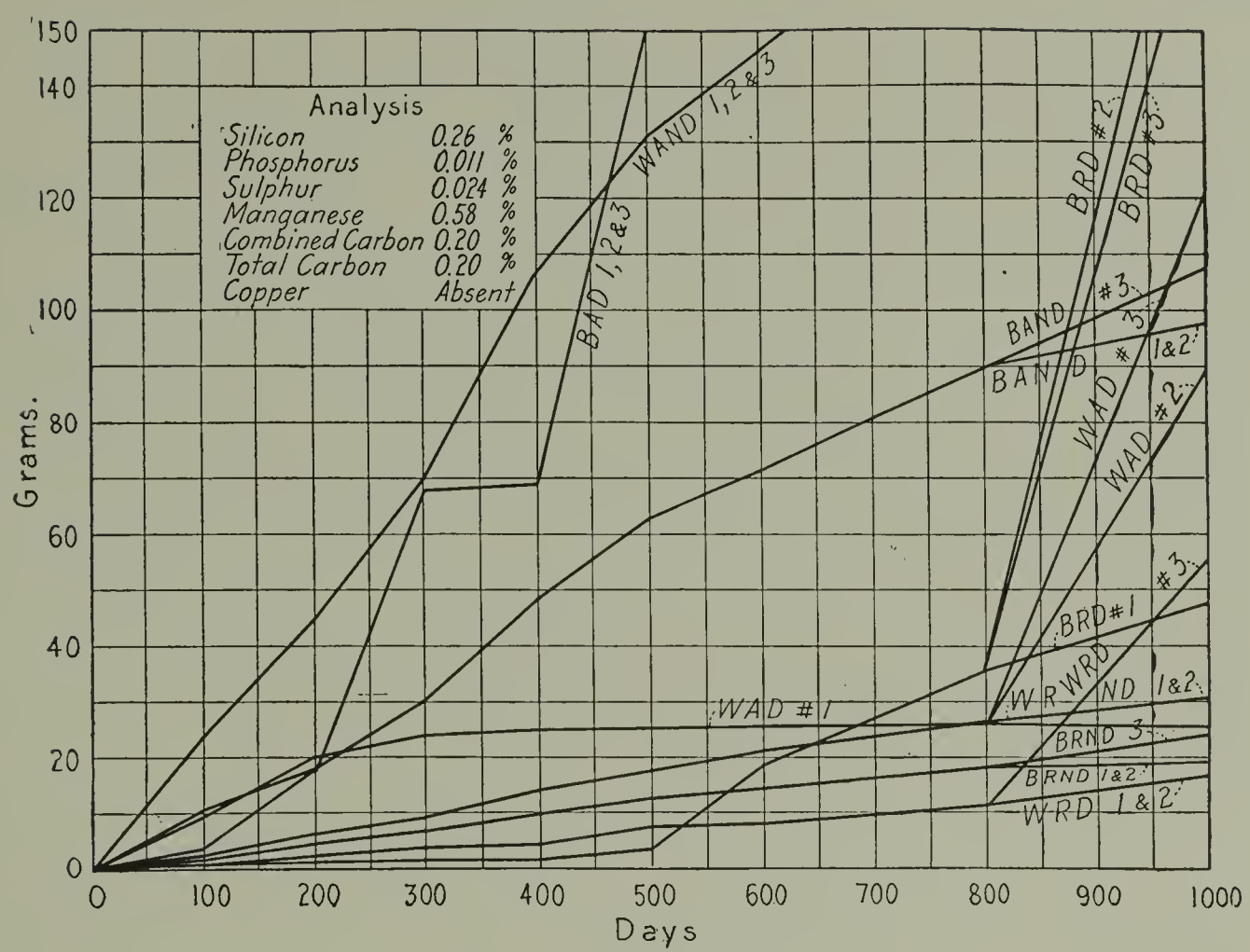

CHART 22.—PP Cast Steel.

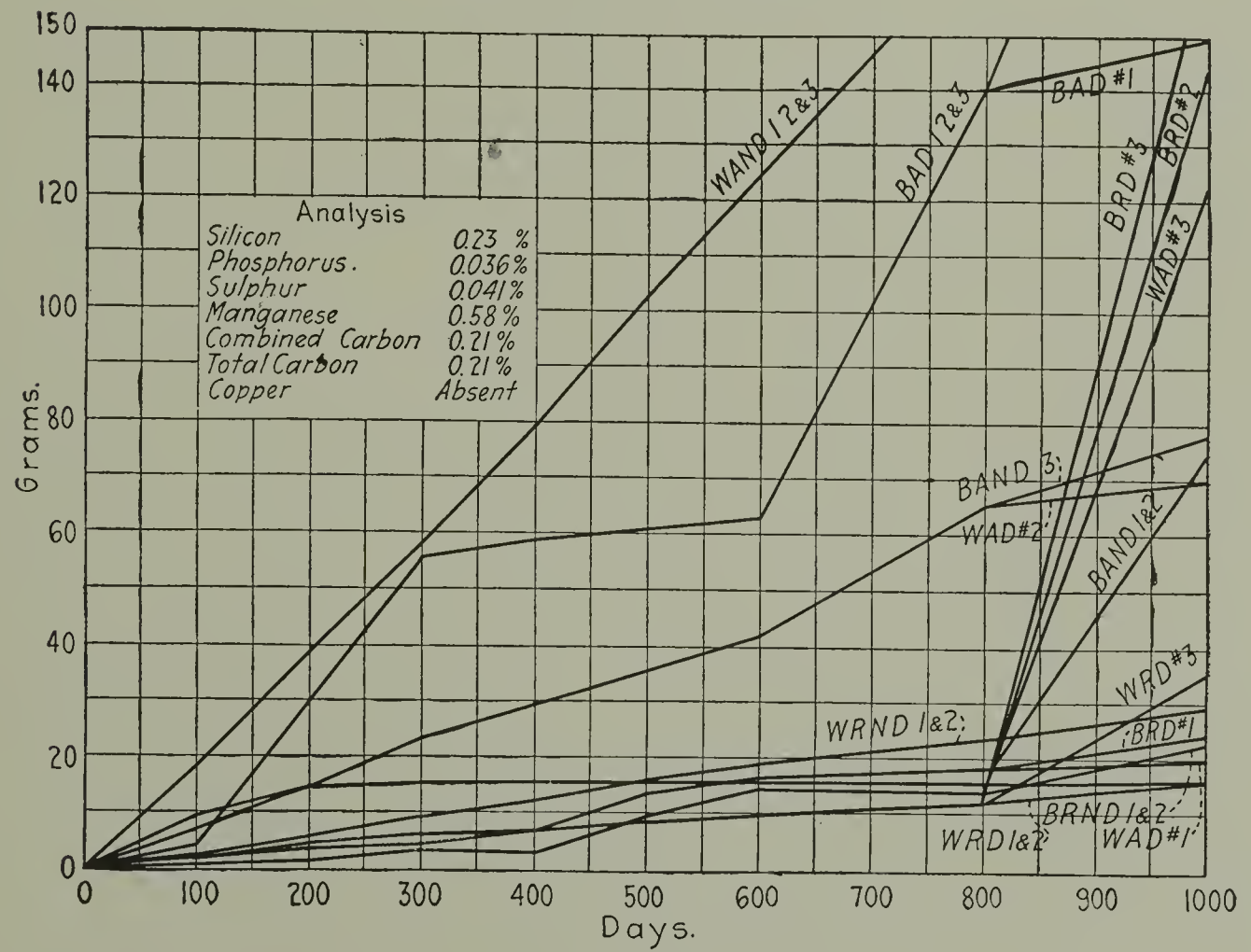

CHART 23.—QQ Cast Steel.

Conditions Causing Least Corrosion

The conditions causing least corrosion, considering all samples, were the following in order of increase:

Condition 5, B. R. N. D., 1, W. R. N. D., and 2, W. R. D.

The first two of these maintained a clean surface throughout the experiment and having only a limited supply of oxygen did not corrode rapidly. Atmospheric oxygen is less soluble in 10 per cent salt brine than in air and it is believed that because of this fact condition 5, B. R. N. D., produced less corrosion than 1, W. R. N. D. Condition 2, W. R. D., produced a layer of magnetic oxide on the surface which adhered tightly in practically all cases. Corrosion did proceed underneath its surface to some extent producing a fine pitting. Both the rolled metals and the cast metals behaved nearly alike under the above three conditions.

Conditions Causing Most Corrosion

Considering all samples, condition 8, B. A. D., was the most destructive, not only causing a great loss of metal but also resulting in deep pitting and perforation of the plates. Next in order and running a close second was condition 3, W. A. N. D., which caused bad pitting where mill scale adhered in patches, but was not inclined to produce pitting in other cases. Except in those cases where mill scale persisted, the surface of the plates under this condition remained clean and under the influence of the supply of air, always present, corrosion proceeded rapidly and rather uniformly.

Condition 4, W. A. D., came third for the rolled metals, fourth for the cast steels and fifth for the other cast plates. Apparently adherent rust, accelerating in some cases, protective in others (particularly the cast metals) caused the marked differences in behavior. This condition more than any other favored the production of rust and scale, and hence produced varying results.

TABLE X

Order of Corrodibility for all Plates in Series 4 Experiments

1 BB	2 CC	3 BB	4 II
5. B. R. N. D.	5. B. R. N. D.	5. B. R. N. D.	1. W. R. N. D.
1. W. R. N. D.	1. W. R. N. D.	1. W. R. N. D.	5. B. R. N. D.
2. W. R. D.	2. W. R. D.	2. W. R. D.	2. W. R. D.
7. B. A. N. D.	7. B. A. N. D.	7. B. A. N. D.	7. B. A. N. D.
6. B. R. D.	6. B. R. D.	6. B. R. D.	6. B. R. D.
3. W. A. N. D.	4. W. A. D.	4. W. A. D.	4. W. A. D.
4. W. A. D.	3. W. A. N. D.	3. W. A. N. D.	3. W. A. N. D.
8. B. A. D.	8. B. A. D.	8. B. A. D.	8. B. A. D.

5 JJ	6 KK	7 UU	8 WW
5. B. R. N. D.	5. B. R. N. D.	5. B. R. N. D.	5. B. R. N. D.
1. W. R. N. D.	1. W. R. N. D.	1. W. R. N. D.	1. W. R. N. D.
2. W. R. D.	2. W. R. D.	2. W. R. D.	2. W. R. D.
6. B. R. D.	7. B. A. N. D.	7. B. A. N. D.	7. B. A. N. D.
4. W. A. D.	6. B. R. D.	4. W. A. D.	6. B. R. D.
7. B. A. N. D.	4. W. A. D.	6. B. R. D.	4. W. A. D.
8. B. A. D.	3. W. A. N. D.	3. W. A. N. D.	8. B. A. D.
3. W. A. N. D.	8. B. A. D.	8. B. A. D.	3. W. A. N. D.

9 TT	10 VV	11 DD	12 EE
5. B. R. N. D.	5. B. R. N. D.	5. B. R. N. D.	5. B. R. N. D.
1. W. R. N. D.	1. W. R. N. D.	1. W. R. N. D.	1. W. R. N. D.
2. W. R. D.	2. W. R. D.	2. W. R. D.	2. W. R. D.
7. B. A. N. D.	7. B. A. N. D.	7. B. A. N. D.	4. W. A. D.
4. W. A. D.	6. B. R. D.	4. W. A. D.	6. B. R. D.
6. B. R. D.	4. W. A. D.	6. B. R. D.	7. B. A. N. D.
3. W. A. N. D.	8. B. A. D.	3. W. A. N. D.	8. B. A. D.
8. B. A. D.	3. W. A. N. D.	8. B. A. D.	3. W. A. N. D.

13 XX	14 FF	15 SS	16 LL
5. B. R. N. D.	5. B. R. N. D.	5. B. R. N. D.	2. W. R. D.
1. W. R. N. D.	2. W. R. D.	1. W. R. N. D.	5. B. R. N. D.
2. W. R. D.	1. W. R. N. D.	2. W. R. D.	1. W. R. N. D.
7. B. A. N. D.	4. W. A. D.	4. W. A. D.	4. W. A. D.
6. B. R. D.	3. W. A. N. D.	6. B. R. D.	6. B. R. D.
8. B. A. D.	7. B. A. N. D.	3. W. A. N. D.	7. B. A. N. D.
4. W. A. D.	6. B. R. D.	7. B. A. N. D.	8. B. A. D.
3. W. A. N. D.	8. B. A. D.	8. B. A. D.	3. W. A. N. D.

TABLE X—*Continued*

17 OO	18 MM	19 NN	20 GG
5. B. R. N. D.	5. B. R. N. D.	5. B. R. N. D.	5. B. R. N. D.
2. W. R. D.	1. W. R. N. D.	1. W. R. N. D.	2. W. R. D.
2. W. R. N. D.	1. W. R. D.	2. W. R. D.	1. W. R. N. D.
4. W. A. D.	4. W. A. D.	4. W. A. D.	4. W. A. D.
6. B. R. D.	6. B. R. D.	6. B. R. D.	6. B. R. D.
7. B. A. N. D.	7. B. A. N. D.	7. B. A. N. D.	3. W. A. N. D.
3. W. A. N. D.	8. B. A. D.	8. B. A. D.	7. B. A. N. D.
8. B. A. D.	3. W. A. N. D.	3. W. A. N. D.	8. B. A. D.

21 RR	22 PP	23 QQ
5. B. R. N. D.	5. B. R. N. D.	5. B. R. N. D.
2. W. R. D.	1. W. R. N. D.	1. W. R. N. D.
1. W. R. N. D.	2. W. R. D.	2. W. R. D.
4. W. A. D.	7. B. A. N. D.	7. B. A. N. D.
6. B. R. D.	4. W. A. D.	4. W. A. D.
3. W. A. N. D.	6. B. R. D.	6. B. R. D.
7. B. A. N. D.	3. W. A. N. D.	8. B. A. D.
8. B. A. D.	8. B. A. D.	3. W. A. N. D.

Chief Differences Between Rolled and Cast Metals under all Conditions

The principal difference between the two classes of metals, rolled and cast, will appear from an inspection of Table X, which shows the order of corrodibility for all samples. This difference lies in the relative position of condition 7, B. A. N. D., 6, B. R. D. and 4, W. A. D. Condition 7, B. A. N. D. occupies position 4 in order of corrodibility for the rolled metals but on the other hand occupies position 6 in the case of the majority of the cast metals. Conversely condition 4, W. A. D., occupies position 4 in the case of the cast metals and position 6 with the rolled. In the case of the samples of cast steel there is still another arrangement slightly different from that of the rolled metals. In the cast steels, condition 4, W. A. D., occupies position 5 and condition 6, B. R. D., occupies position 6. The reverse of this sequence is true for the rolled metals. In other respects the cast steel samples follow the order of corrodibility set down for the rolled products. All of these points are brought out in the following table:

Usual Order of Corrodibility

Position	Rolled Metals	Cast Steels	Other Cast Metals
	Least		Least
1.	5. B. R. N. D.		5. B. R. N. D.
2.	1. W. R. N. D.		1. W. R. N. D.
3.	2. W. R. D.		2. W. R. D.
4.	7. B. A. N. D.	7. B. A. N. D.	7. B. A. N. D.
5.	6. B. R. D.	6. B. R. D.	6. B. R. D.
6.	4. W. A. D.	4. W. A. D.	4. W. A. D
7.	3. W. A. N. D.		3. W. A. N. D.
8.	8. B. A. D.		8. B. A. D.
	Most		Most

Corrosion of Aluminium and Copper

In order to obtain a comparison between aluminium and copper, rolled plates of each of these metals, 16 gauge, were subjected to the same corroding influence as the samples of iron in the No. 4 Series of experiments and the results are tabulated in Table XVI. The aluminium plates used contained 0.08 per cent copper, 0.50 per cent silica and 0.29 per cent iron. These experiments were continued for 905 days only instead of 1000. The condition of the plates at the end of the experiment is described below:

Condition of Aluminium Plates after 905 Days

Water at Rest, not Dried.—Original luster remaining over most of surface, mottled by white patches and a few reddish patches (iron?)

Water at Rest, Dried.—Same as above, but surface slightly duller.

Water, Air Agitation, not Dried.—Same as above, but more signs of pitting.

Water, Air Agitation, Dried.—Same as water, air agitation, not dried, but slightly duller surface.

Ten Per Cent Brine at Rest, not Dried.—Surface dull, finely mottled with products of corrosion. A few large pits near edges. Very fine raised black pin points scattered over surface (copper? iron?)

Ten Per Cent Brine at Rest, Dried.—Same as not dried.

Ten Per Cent Brine, Air Agitation, not Dried.—Same as above.

Ten Per Cent Brine, Air Agitation, Dried.—Same as above, but somewhat more products of corrosion on surface.

Condition of Copper Plates after 905 Days

Water at Rest, not Dried.—Surface smooth black with greenish cast, a little original luster remaining.

Water at Rest, Dried.—Same as above, but duller.

Water, Air Agitation, not Dried.—Surface black with greenish tinge, some of original luster remaining.

Water, Air Agitation, Dried.—Same as above but duller.

Ten Per Cent Brine at Rest, not Dried.—Uniform, smooth, thin, tightly adhering coating of malachite green color.

Ten Per Cent Brine at Rest, Dried.—Same as above, but somewhat rougher.

Ten Per Cent Brine, Air Agitation, not Dried.—Same as 10 per cent brine at rest, not dried.

Ten Per Cent Brine, Air Agitation, Dried.—Same as above, but somewhat rougher.

The aluminium plates lost practically no weight worth mentioning under any of the eight conditions although there were definite signs of corrosion in some instances, particularly in 10 per cent brine in the form of white deposits at various points on the plates and a few deep pits. The losses from copper, particularly under conditions 5, 6, 7 and 8, in all of which brine was used, were much more considerable than the losses from aluminium.

It has been stated by Walker[1] that "the aluminium oxide coat on metallic aluminium, effectually protects the metal and practically prevents further corrosion." This does not appear to be the case (unless the oxide layer is submicroscopic or of a passive nature), since much of the original metallic polish or luster remained on the aluminium plates in the above experiment to the last, particularly those in water. The absence of corrosion in the aluminium plates was apparently due to some other cause than adherence of the products of corrosion.

It is needless to point out that copper is strongly electro-negative to aluminium and on the basis of the electrolytic theory which takes into consideration solution tension alone, aluminium should corrode much more rapidly than copper and also more rapidly than iron, but solution tension is only one factor in corrosion and in some cases a very minor factor.

[1] Scientific American 122, 110, January, 1920.

TABLE XVII

CORROSION OF ALUMINIUM AND COPPER

6×6 in. Plates

Loss in Grams

ALUMINIUM:

Age. in Days.	Water at Rest.		Water, Air Agitation.		10% Brine at Rest.		10% Brine Air Agitation.	
	N. D. Av.	D. Av.	N. D. Av.	D. Av.	N. D. Av.	D. Av.	N. D. Av.	D. Av.
100	.3	.3	.2	.3	.0	.0	.0	.0
200	.1	.1	.1	.1	.0	.0	.0	.0
300	.0	.0	.0	.0	.0	.0	.0	.0
400								
500	.0	.....	.1					
600	.0							
800	.0	.....	.....	.3				
905	.0	.0	.4	.1	.1	.8	.2	.5
COPPER:								
100	.0	.0	.0	.0	2.1	1.1	3.4	3.4
200	.1	.0	.0	.0	4.0	2.6	4.6	4.0
300	.1	.0	.5	.4	5.8	3.8	5.2	5.0
400	.1	.0	.6	.4	6.4	4.5	6.2	6.2
500	.1	.0	.7	.5	9.2	5.9	9.7	9.6
600	.1	.1	.7	.5	10.7	6.9	11.2	10.4
800	.1	.1	.3	.6	13.5	8.3	12.1	10.0
905	.1	.1	.3	.7	14.0	8.3	12.4	10.0

N. D.—Not dried. D.—Dried in air semi-weekly.

The copper plates lost more in water with air agitation than without, although the losses in both cases were very small. In brine the losses were much greater but were less when the samples were dried than when not dried, thus suggesting a slight protective action of the products of corrosion in the case of the dried samples.

If we consider that oxygen accelerates corrosion merely by removing the hydrogen film produced by solution pressure in the first instance, it is difficult to see why the corrosion of aluminium should proceed at so much slower a rate than iron and doubly hard to understand why the corrosion of copper should proceed at a more rapid rate than that of aluminium. There is the possible explana-

tion that iron and copper catalyze the oxygen-hydrogen reaction more than does aluminium or that the ferric hydrate (rust) produced catalyzes this reaction but there appears to be more than this involved in the different behavior of the three metals, aluminium, iron and copper.

SUMMARY

1. When any of the ordinary varieties of iron or steel corrode under ordinary conditions, oxygen determines the commencement of the corrosion.

2. External conditions overbalance composition in most cases in determining the course of corrosion.

3. The role of oxygen appears to be that of a depolarizer since it combines not only with hydrogen at the corrosion cathodes but also with ferrous iron at the corrosion anodes.

4. The role of carbon dioxide is a minor one in the corrosion of iron, under ordinary circumstances.

5. Rust plays several important roles, accelerating corrosion by acting as a cathode and probably as a depolarizer and in other cases where it adheres strongly it acts as a protector. It is a frequent cause of deep pitting.

6. Mill scale when it adheres tightly and uniformly may protect iron and steel against corrosion for a time at least but where it adheres locally in patches it is a cause of deep pitting.

7. In the absence of oxygen corrosion commences but soon stops or drops to a negligible rate.

8. In salt solutions corrosion follows a course depending principally on the amount of oxygen in solution, secondly on the influence of the salt solution.

9. Oxygen causes much more rapid corrosion than air but may produce a protective layer of rust not produced in air, thus reducing corrosion below that in air under similar conditions.

10. Corrosion of 12 common varieties of iron and steel carried out under 8 different conditions for 1000 days is described and tabulated in detail. It is difficult to summarize this data and reference should be had to the text.

13. Pure iron corrodes relatively slowly under non-oxidizing conditions or with limited access of oxygen and relatively rapidly in the presence of oxygen or air.

14. Whereas cast iron corrodes relatively more in the absence of air or oxygen, or with limited supply, and relatively less in the presence of air or oxygen compared with the purer irons.

15. The production of an iron which will resist corrosion because of its purity is impossible of attainment. Such an iron would resist corrosion fairly well if submerged and in situations which allow but limited supply of oxygen. However, under ordinary conditions oxygen (air) is present and pure irons in the presence of air corrode with extreme rapidity.

16. In many cases rust acts as a protector of iron in exposed situations but the correlation between rust-adhesion and composition is not yet sufficiently worked out.

17. Generally speaking, rust adheres better to cast iron than to pure rolled iron and hence in exposed situations cast iron withstands corrosion better than purer open hearth or puddled irons.

18. When "busy iron" fails to corrode it is because of 1. Polished surfaces. 2. Protective rust. 3. Accidental coating of oil.

19. Solution pressure while fundamental in corrosion phenomena is not as a rule the determining factor.

20. A comparison of the corrosion of aluminium and copper plates with the corrosion of 12 common varieties of iron and steel shows that aluminium (with a high solution pressure) corrodes practically not at all under any of the 8 conditions to which it was subjected; and corrodes not only very much less than iron under the same circumstances but even less than copper, a semi-noble metal with low solution pressure.

21. For a general theory of corrosion many factors must be taken into consideration, among which solution pressure may be, relatively a minor one.

RATES OF SOLUTION OF IRON AND STEEL IN NON-OXIDIZING AND OXIDIZING ACIDS

By WILLIAM D. RICHARDSON

Read at the Montreal Meeting, June 29, 1920

A SERIES of samples of iron and steel whose comparative corrodibility under eight different conditions had been determined during a period of 1000 days, was subjected to the action of normal sulphuric, hydrochloric and nitric acids and the relative loss in these acids obtained for comparison with losses under the other conditions of corrosion.[1] These samples of iron and steel are referred to as Series 4 and the various kinds used in the experiments and their analyses are shown in Table I. All of the pieces tested were identical with those used in the corrosion experiments of Series 4 previously reported and measured 6×6 inches square, some of them being No. 16 iron and the cast metals $\frac{1}{8}$ inch thick. For the acid solution tests, the plates were all surfaced by means of the sand blast followed by treatment with fine emery cloth and the surfaces were made as nearly uniform as possible. A temperature of 16° was maintained except in the case of nitric acid as noted.

There is a certain resemblance between the corrosion which takes place when plates are submerged in water and brine when a minimum quantity of atmospheric oxygen is present and that which occurs when metals dissolve in the ordinary non-oxidizing acids such as sulphuric and hydrochloric. This resemblance, however, while characteristic in a general way, may not hold good at all points because of one essential difference in the two conditions compared. In the case of conditions 1 and 5,[2] water and brine respectively, at rest, there is always present a small amount of oxygen to influence the course of corrosion, whereas when the samples are submerged in a non-oxidizing acid, the latter is quickly relieved of its dissolved oxy-

[1] See preceding paper "Experiments on the Corosion of Iron and Steel."

[2] See preceding paper.

gen and henceforward the only gas present in solution is hydrogen resulting from the action of the metal on the acid and perhaps small quantities of other gases arising from impurities in the metal.

TABLE I

COMPOSITION OF IRONS USED IN SERIES 4 EXPERIMENTS

		Silicon, Per Cent.	Phosphorus. Per Cent.	Sulphur, Per Cent.	Manganese, Per Cent.	Total Carbon, Per Cent.	Graphitic Carbon, Per Cent.	Combined Carbon, Per Cent.	Copper, Per Cent.
AA	Copper bearing.....	.04	.007	.015	.063	.059	....	.059	.12
CC	Copper bearing.....	.03	.005	.016	.16	.056	....	.056	.10
BB	Open-hearth pure iron.	.04	.008	.015	.024	.030	....	.030	.015
II	Open-hearth pure iron.	.002	Trace	.019	.002	.020	....	.020	.023
JJ	Ditto cold rolled.....	.007	.002	.016	.023	.020	....	.020	.025
KK	Ditto cold rolled.....	.008	.002	.013	.020	.030	....	.030	absent
UU	Open-hearth iron.....	.008	.015	.043	.433	.164	....	.164	.021
WW	Open-hearth iron.....	.004	.020	.041	.282	.096	....	.097	.030
TT	Bessemer iron.....	.005	.075	.029	.450	.119	....	.119	.030
VV	Bessemer iron.....	.008	.025	.033	.407	.132	....	.132	.020
DD	Genuine puddled iron.	.14	.12	.014	.31	.023	....	.023	absent
EE	Genuine puddled iron.	.15	.17	.019	.030	.030	....	.030	Trace
XX	Charcoal iron.....	.003	.052	.013	.029	.060	....	.060	.047
FF	Gray cast iron.....	2.71	.82	.120	.32	3.21	2.62	.59	absent
SS	Gray cast iron.....	2.24	.40	.122	.44	3.08	2.67	.41	absent
LL	White cast iron.....	.81	.137	.054	.251	1.35	0.05	1.30	absent
OO	White cast iron.....	.48	.143	.044	.216	1.55	0.05	1.50	absent
MM	Malleable iron.....	.90	.134	.09	.25	.57	0.50	.07	absent
NN	Malleable iron.....	.77	.164	.067	.26	2.44	1.44	1.00	absent
GG	Semi-steel.....	2.95	.92	.110	.33	3.06	2.72	.34	absent
RR	Semi-steel.....	2.15	.327	.121	.46	3.15	2.35	.80	absent
PP	Cast steel.....	.26	.011	.024	.58	.20	....	.20	absent
QQ	Cast steel.....	.23	.036	.041	.58	.21	....	.21	absent
YY	Duriron.....	15.00	(approximately)						

The first series of acid corrosion tests was undertaken with the idea of determining the different rates of solution for the various metals used in Series 4 corrosion experiments in a non-oxidizing acid such as sulphuric, and also in an oxidizing acid such as nitric. The results are shown in Table II, which is condensed from a larger table

TABLE II

COMPARATIVE RATES OF SOLUTION OF IRON AND STEEL IN SULPHURIC AND NITRIC ACIDS

		H_2SO_4 Av. per Hr. First 20 Hrs.	HNO_3 Av. per Hr. 2 Hrs.	H_2SO_4 Av. per Hr. Second 20 Hrs.
AA	Copper bearing	.09	19.0	.03
CC	Copper bearing	.23	19.8	.00
BB	Open-hearth pure iron	.29	18.8	.03
II	Open-hearth pure iron	.30	20.5	.04
JJ	Open-hearth pure iron	.08	20.7	.05
KK	Open-hearth pure iron	.10	20.2	.04
UU	Open-hearth iron	.19	15.2	.02
WW	Open-hearth iron	.30	19.6	.05
TT	Bessemer	.34	20.5	.09
VV	Bessemer	.27	14.7	.01
DD	Puddled iron	.39	20.0	.06
EE	Puddled iron	1.03	18.2	.86
XX	Charcoal iron			
FF	Gray cast iron	4.82	5.0	5.02
SS	Gray cast iron	4.87	8.8	3.99
LL	White cast iron	2.12	9.9	2.33
OO	White cast iron	2.03	6.5	1.77
MM	Malleable iron	2.91	5.4	.98
MM	Malleable iron	1.56	6.0	1.36
GG	Semi-steel	4.18	5.4	5.15
RR	Semi-steel	4.06	7.2	4.26
PP	Cast steel	.66	16.5	.30
QQ	Cast steel	1.03	16.0	.77

not printed here. Normal acids were used and for the tests in normal sulphuric acid the temperature was maintained at 16° C. As will be explained later the temperature could not be controlled in nitric acid and went much higher than 16° C. The plates were first subjected to the action of normal sulphuric acid, then to the action of normal nitric acid, and again to the action of normal sulphuric acid. They were first placed in normal sulphuric acid for one hour. This removed practically all the mill scale. They were then returned to the same acid for another period of four hours. Then successively five-hour periods until a total of twenty hours was reached. They

were then placed in normal nitric acid for one hour, but the temperature rose rapidly to 39° C. After weighing they were again placed in fresh normal nitric acid which was cooled as well as possible in a chill room and by contact with ice but in spite of these precautions the temperature ran up to 30° C. Therefore, the results in nitric acid cannot be compared directly to the results in sulphuric. Finally the plates after weighing were again placed in normal sulphuric acid for a total period of twenty hours. An inspection of Table II indicates that both in the first and second sulphuric acid tests the rolled plates show much less loss than the cast plates. Among the rolled sheets, Puddled Iron EE showed a comparatively high loss and the two samples of cast steel, PP and QQ relatively small losses. With these partial exceptions the statement holds with greater force that the cast metals lost much more weight than the rolled metals. This was also true in conditions 1 and 5 corrosion tests, water and brine respectively at rest, the plates not being dried.

In the second sulphuric acid test the rate of loss was less for the rolled sheets than in the first period and this also held as a rule for the cast metals although there were numerous important exceptions. Sample MM, Malleable Iron, appeared in this test to be so heterogeneous in composition that it cannot be taken into account. The samples of cast steel, PP and QQ, lost distinctly less the second time than the first time.

The figures in nitric acid cannot be compared directly with those in sulphuric acid on account of the rise in temperature noted, but the relative rates can be compared, and one notes with astonishment that the rolled metals which dissolve less readily in sulphuric acid than the cast metals dissolve much more readily than the latter in nitric acid. In fact, practically all the samples that dissolve at a relatively slow rate in the non-oxidizing sulphuric acid dissolve at a relatively high rate in the oxidizing nitric acid. In this respect the cast steel samples PP and QQ behaved somewhat as the rolled metals.

It appeared from this first series of experiments, particularly the results in nitric acid, that a way had been discovered for the correlation of accelerated corrosion tests in acid with service tests in the presence of air and an important means of experiment devised for the further study of corrosion from a new angle of view. If the results in non-oxidizing acids as compared with oxidizing acids could be correlated with various results obtained under the conditions of the No. 4 series of experiments, a key might have been found to much that

had hitherto been mysterious in connection with corrosion. It appeared further that the results might be explained in some way by the effects of polarization and depolarization. It is well-known that pure iron in dilute non-oxidizing acids becomes saturated at the surface with occluded hydrogen and the polarizing effect of the hydrogen may very well reduce or prevent further action of the acid. On the other hand, an impure metal such as a gray cast iron may dissolve in weak acids in such a way that much of the hydrogen comes off on graphitic carbon surfaces or other impurities so that ferrite areas become less saturated with occluded hydrogen and there is less tendency to polarization and stoppage of the acid corrosion. In nitric acid the purer irons and perhaps rolled metals generally would have no opportunity to become polarized and with their large ferrite areas solution would go on at a relatively rapid rate. The solution of the cast metals in nitric acid would not be accelerated by the oxidizing action of nitric acid to the same extent as purer metals.

The course by which a surface of pure iron becomes inactive by occlusion of hydrogen may be imagined to be somewhat as follows: In the beginning certain areas are positive and others negative, the latter being associated with occluded oxygen or an oxidized condition. By the action of hydrogen, the oxygen or oxides of such negative areas are reduced and may become positive, with resulting reversal of polarity. Whenever such a reversal over varying areas may occur, the galvanic action becomes weaker and weaker as the current swings back and forth, until at last enfeebled to the vanishing point electrolysis ceases altogether until reactivated by access of oxygen.

The results show how little confidence can be placed in the accelerated corrosion tests heretofore proposed.

Since every condition of corrosion apparently has its own rate, the results obtained held only for the conditions of the experiment.

The rapid rise of temperature in the nitric acid could only be due to the oxidation of hydrogen and of ferrous salts.

Correlation of Corrosion Tests and Acid Tests on Series 4 Samples

An attempt at correlation between acid solution and corrosion under the conditions of the Series 4 experiments is indicated in the following table:[1]

Acid Solution	Corrosion
H_2SO_4	W. N. O.
	W. R. N. D.
	B. R. N. D.
HNO_3	W. A. N. D.
	B. A. N. D.
	W. A. D.
	B. A. D.
H_2CrO_4	W. R. D.

B. R. D. not placed.

The initials W. N. O. stand for Water, No Oxygen, and represent a condition similar to that maintained in the experiments of Whitney, Friend, Cushman[2] and others in determining the action of pure water on iron.

[1] The eight conditions of corrosion together with the abbreviations used for them, made use of in the preceding paper entitled "Experiments on the Corrosion of Iron and Steel," are as follows:

1. W. R. N. D. Water at rest, not dried.
2. W. R. D. Water at rest, dried semi-weekly.
3. W. A. N. D. Water with air agitation, not dried.
4. W. A. D. Water with air agitation, dried semi-weekly.
5. B. R. N. D. Brine at rest, not dried.
6. B. R. D. Brine at rest, dried semi-weekly.
7. B. A. N. D. Brine with air agitation, not dried.
8. B. A. D. Brine with air agitation, dried semi-weekly.

The reader is referred to this paper for a more complete exposition of the various conditions of corrosion.

[2] Bull. 30 U. S. Dept. Agr. 1907.

Solution in a non-oxidizing acid (under the conditions laid down) such as sulphuric corresponds most closely to corrosion in pure water. Now as is well-known, corrosion in pure water proceeds at a very slow pace or to speak more accurately is soon brought to a halt either by the formation of a Helmholtz double layer or by polarization. The resistance of pure water is considerable and the electrolytic currents concerned in corrosion feeble. On the other hand in a non-oxidizing acid corrosion proceeds much more rapidly although there exists nevertheless a tendency toward slowing down of the electrolytic action owing to polarization. In sulphuric acid, impure metals such as gray cast iron, dissolve more rapidly than purer metals such as pure open-hearth iron and it might be expected that this same condition would hold in the case of water. Experiments to demonstrate this were carried out with doubtful results. The amounts of iron entering solution in water in the absence of air both from cast metals and pure rolled metals were so small as to preclude accurate comparison.

Solution of various kinds of iron in nitric acid shows a certain correspondence to corrosion which proceeds in such a way that a clean iron surface is maintained while an abundance of free oxygen is provided. Such conditions are found in 3, W. A. N. D. and 7, B. A. N. D. Conditions 1, W. R. N. D. and 5, B. R. N. D., correspond to a position, as regards acid solution, lying midway between solution in non-oxidizing acid such as sulphuric and an oxidizing acid such as nitric.

Chromic acid even at low concentrations produces passivity of an iron surface and puts an end to solution or corrosion. A certain correspondence is observable between this condition and an iron protected by a closely adhering oxide layer such as that formed under condition 2, W. R. D.

Between solution in weak nitric acid and the effect of passivity as produced by chromic acid or strong nitric are correlated those conditions of corrosion which bring about a more or less adherent layer of rust which in some cases may act as an accelerator of corrosion and in others may protect by its adhesion to the iron.

Condition 6, B. R. D., is not placed in the above scheme although it corresponds most closely to condition 2, W. R. D. However, condition 6, B. R. D., fails to produce a layer of adherent rust and the iron surface is maintained clean owing probably to the ability of brine to lift any layer of oxides formed on the surface.

Thus it is seen that there is at least a rough correspondence as indicated in the above table between solution in acids and corrosion under various conditions when less or more oxygen is present. This correlation amounts to more than a superficial resemblance and although the scheme as suggested above may be only the bare approximation to the principle, there is no doubt that some such relationship can be worked out which should prove useful as an aid to the investigation of corrosion phenomena.

An interesting comparison can be made between corrosion of the cast metals under conditions 3, W. A. N. D., and 7, B. A. N. D., and solution in nitric acid. The results are shown in the following table:

TABLE IIA

COMPARISON OF CORROSION UNDER CONDITIONS 3, W. A. N. D., AND 7, B. A. N. D. WITH SOLUTION IN NITRIC ACID FOR CAST METALS

		Loss of Weight in Grams. 1000 Days.		One Hour. Normal Nitric Acid.
		3, W. A. N. D.	7, B. A. N. D.	
FF	Gray cast iron	78.8	88.1	5.0
SS	Gray cast iron	103.4	143.5	8.8
LL	White cast iron	230.7	116.2	9.9
OO	White cast iron	144.1	103.0	6.5
MM	Malleable iron	222.2	118.5	5.4
NN	Malleable iron	218.3	113.1	6.0
GG	Semi-steel	97.3	124.0	5.4
RR	Semi-steel	118.6	124.5	7.2
PP	Cast steel	242.2	107.4	16.5
QQ	Cast steel	247.6	78.5	16.0

These figures show that for many of the samples the comparative rates of corrosion in the presence of air and the rate of solution in normal nitric acid are similar. Thus of the two gray cast irons, FF shows a lower rate of corrodibility and a lower rate of solution than SS. The same rule holds for the two white cast irons, the two semi-steels and approximately for the two samples of cast steel whose rates of corrosion and of solution in nitric acid are very much alike. The rates for corrosion and acid solution of the two samples of malleable iron are reversed but the rates are so nearly alike that the acid rates

might be in accord with the corrosion rates in another test. Certain differences were bound to develop between conditions 3 and 7 and solution in nitric acid since under condition 3 adherent rust exerted a disturbing influence in several instances whereas the surfaces of the plates under condition 7 were reasonably clean and when dissolving in nitric acid still more so except for the residue consisting chiefly of graphite remaining with some samples.

Another test was made on four samples only:

CC Copper-bearing Iron
BB Open-hearth Pure Iron
SS Gray Cast Iron
GG Semi Steel

All four samples were first pickled to remove mill or foundry scale, then placed in normal sulphuric acid at 16° for five hours and weighed. They were then immersed in normal hydrochloric acid for five hours and weighed after ordinary cleaning and again after sand blasting. They were then placed in normal nitric acid for three hours at 16° and again weighed before and after sand blasting. The reason for sand blasting was the accumulation of a closely adherent layer, apparently consisting of graphite, on the surface of the cast metals. This deposit had been noticed before and had been removed before weighing as well as possible but it adhered so tightly that it was thought best in this instance to remove it by the sand blast. The results are given below

TABLE III

Loss in Grams from Plates 6×6 inches Square.

	H_2SO_4 5 Hrs.	HCl 5 Hrs.	After Sand Blasting.	HNO_3 3 Hrs.	After Sand Blasting.
CC Copper bearing	.1	.1	.1	85.8	85.8
BB Open-hearth pure iron	.0	.6	.6	86.9	86.9
SS Gray cast iron	32.3	43.5	14.8	50.2	8.0
GG Semi-steel	23.7	26.8	17.7	48.0	11.8

Calculating the losses per hour and dividing the losses after the first sand blasting equally between the losses in sulphuric and hydrochloric acids and adding the losses after the second sand blasting to the nitric acid losses, the following results are obtained (Table IV):

TABLE IV

LOSS IN GRAMS PER HOUR FROM PLATES 6×6 INCHES SQUARE. NORMAL ACIDS AT 16° C.

	H_2SO_4	HCl	HNO_3
CC Copper bearing	.02	.02	28.6
BB Open-hearth pure iron	.0	.1	28.9
SS Gray cast iron	7.9	10.2	19.4
GG Semi-steel	6.5	7.1	19.9

In this test as in the previous one, the non-oxidizing acids produce very little loss in the case of the rolled metals and moderate losses, on the other hand, in the case of the cast metals, but when the same plates are immersed in nitric acid the rolled metals show a high rate of loss with the cast metals below them. The considerable losses in nitric acid from the cast metals especially after sand blasting, include not only metal dissolved, but also graphite and other impurities and metal mechanically dislodged and removed with the graphite.

When the plates are introduced into a non-oxidizing acid there is a rapid evolution of gases from the cast metals and practically no evolution of gases from the rolled metals. When the plates are introduced into the nitric acid there is also a rapid evolution of gases from the cast plates. No gases are evolved from the rolled metals but the fact that they are going rapidly into solution can be easily observed, inasmuch as a stream of ferric nitrate, known by its dark color, is constantly flowing from their surfaces downward.[1]

The course of solution in nitric acid in the case of the pure rolled metals as contrasted with the cast metals appears to be decidedly and fundamentally different. No hydrogen or other gas is evolved from the rolled plates whereas there is rapid and continuous effervescence from the cast metals. This must have a real significance in connection with corrosion.

Another test was made on the same group of four plates, CC, BB, SS and GG. In this case the plates were first prepared by careful sand blasting to remove mill and foundry scale. They were then immersed in normal nitric acid for one hour at 16° C.; taken out, weighed, sand blasted and again weighed. They were then immersed in a fresh lot of normal nitric acid, weighed, sand blasted and weighed again. The results are given in Table V below:

[1] The ferric nitrate appears to contain nitrogen oxides in solution.

TABLE V

LOSS IN GRAMS FROM PLATES 6×6 INCHES SQUARE IMMERSED IN NORMAL NITRIC ACID AT 16° C.

	Loss First Hour.	Total Loss After Sand Blasting.	Loss Second Hour.	Total Loss After Sand Blasting.
CC Copper bearing.....	34.9	34.9	32.8	32.8
BB Open-hearth pure iron...	34.6	34.6	34.8	34.8
SS Gray cast iron.....	15.0	18.3	16.2	18.6
GG Semi-steel.....	14.0	18.6	16.0	18.3

This last test probably represents the best results of the action of nitric acid on comparatively pure rolled metals as contrasted with cast metals. The surfaces in all cases were clean, smooth and had not previously been in contact with acids. The losses of the rolled metals were approximately twice the losses of the cast metals whereas in non-oxidizing acids the losses of the cast metals amounted to from 10 to 20 or even more times the losses from the rolled metals. More extensive work on the solution of metals in various acids, oxidizing and non-oxidizing, ought to yield results of importance to the theory of corrosion.

Several other tests placed the rate of cast iron dissolving in normal nitric acid (16° C.) at approximately half that of the comparatively pure rolled metals.

SOLUTION OF IRON IN SULPHURIC ACID WITH AIR AGITATION

It was thought that if an iron plate was allowed to dissolve in normal sulphuric acid through which a rapid stream of air was kept moving that the rate of solution might be accelerated. Sample II of open-hearth pure iron was selected for the experiment and one of the regular plates, 6×6 inches, was cleaned and submerged in normal sulphuric acid for five hours with air agitation, then five hours without, etc., as shown in the following table:

With better and more abundant aeration such as that which might be furnished by a filtros plate, it is thought that the rate in normal sulphuric acid would be considerably greater.

The presence of air even in limited amount definitely accelerated the rate of solution but not to the extent that was anticipated. The

rate per hour with air agitation amounted to .15 gram and without air agitation to .09. The rate therefore was not quite doubled.

TABLE VI

SOLUTION OF OPEN-HEARTH PURE IRON IN NORMAL SULPHURIC ACID WITH AND WITHOUT AIR AGITATION.

Sample II. Temperature 17–19° C., Average 18° C.

	Weight for each Period.	With Air Agitation, Grams Loss Each Period.	Without Air, Grams Loss Each Period.	With Air Agitation, Av. Loss per Hour.	Without Air, Av. Loss per Hour.
Original sample	289.2				
Five hours with air agitation	288.5	0.7	.....	0.14	
Five hours without air agitation	288.2	.....	0.3	.....	0.06
Five hours with air agitation	287.4	0.8	.....	0.16	
Twenty-four hrs. without air agitation	284.7	.....	2.7	.....	0.11
Twenty-four hours with air agitation	281.1	3.6	.....	0.15	
Eight hours without air agitation	280.7	.....	0.4	.....	0.05
Total average		5.1	3.4	0.15	0.09

CONCLUSION

Relatively pure iron dissolves at a low rate in non-oxidizing acids such as normal sulphuric (and hydrochloric) whereas less pure metals, such as cast iron, white cast iron and malleable iron, dissolve at a relatively high rate, while cast steel dissolves at a rate between the two. On the other hand, in normal nitric acid, the relatively pure metals dissolve at a very high rate while the less pure metals, such as cast iron, white cast iron, malleable iron and semi-steel, dissolve at a much lower rate, and cast steel again occupies a position between the two extremes. Although the difficulties of reproducing exactly identical conditions are great, the results reported appear to be sufficiently comparable to indicate the general rule. Just what impurities in the less pure metals cause the different behavior in non-oxidizing and oxidizing acids has not been definitely proven but undoubtedly carbon (graphite) plays an important part.

A SUGGESTED BASIS FOR AN INDEX OF CORROSION FOR IRON AND STEEL

By WILLIAM D. RICHARDSON

Read at the Montreal Meeting, June 29, 1920

DATA presented in the paper entitled "Rates of Solution of Iron and Steel in Non-oxidizing and Oxidizing Acids," indicate that a sample of pure iron dissolves very slowly in normal sulphuric and hydrochloric acid but comparatively rapidly in normal nitric acid; and that an impure iron such as cast iron dissolves comparatively rapidly in normal sulphuric or hydrochloric but relatively more slowly in normal nitric acid. The reasons for this were discussed to some extent in that paper, and an attempt was made to correlate the rates of solution in non-oxidizing and oxidizing acids with the results of corrosion tests when a limited amount and an abundance of atmospheric oxygen were present, and certain important resemblances between solution in acids and corrodibility were pointed out for several varieties of iron and steel.

In the present paper an attempt will be made to formulate an expression for the corrodibility of a given kind of iron or steel based on its behavior in a non-oxidizing and oxidizing acid. The earlier attempts to develop a so-called accelerated corrosion test by the use of a non-oxidizing acid (sulphuric) alone, resulted in failure.[1] When this test was applied to the purer irons or mild steels a very low index of corrosion was obtained on account of the low rate of solution, but it was found that in service tests under oxidizing conditions that such metals corroded much more rapidly than, for example, cast iron, although the latter dissolved more rapidly in the acid. It should be emphasized that what follows in this paper is offered mainly by way of suggestion as a step toward the desired end, and may prove to be far from perfect, but which will afford at least some indication of the probable behavior of a given sample under both non-oxidizing and oxidizing conditions of

[1] Proc. Soc. Test. Mat. 7, 209, 1907.

corrosion. For the basic tables, data and discussion, the reader is referred to the papers already mentioned. These data will not be repeated here, but on the other hand the fundamental conditions will be discussed and directions given for one method of procedure. This method is subject to modification and improvement after trial in different hands and the accumulation of more extensive data than the writer has been able to gather up to the present time.

Condition of the Surface

This is all important in any corrosion test. Rust and mill scale should be removed by pickling, sand blasting or machining. A smoothly machined surface is probably the best for the purpose but difficult to produce on thin plates. A sand-blasted surface is open to objection on account of the pounding or hammering effect of the sand. Perhaps for all kinds of metal a carefully sand-papered surface produced by mechanical abrasion, for example, by a horizontal grinding wheel or plate, would be as well adapted to the purpose as any. The directions of Cushman's Committee for the preparation of pieces for the accelerated corrosion test are as follows:

"Samples are polished first with No. 00 emery paper and finally with flour emery. The polishing should be done as much as possible so that the polish marks run at right angles to the direction in which the metal was rolled. After polishing, the test pieces should not be handled with the fingers or allowed to come in contact with dirt or grease of any kind."

Size of Test Pieces

The test pieces used by the writer have been 6x6 inches square, practically equivalent to 15×15 cm. The rolled sheets were of No. 16 iron and cast pieces were $\frac{1}{8}$ inch thick or as thin as they could be cast satisfactorily. The Committee of the Society for Testing Materials found that the corrosion of a sample of iron in acid was not directly proportional to the area exposed. The size of the test pieces recommended were 2 inches in length, $\frac{1}{2}$ inch in width and $\frac{1}{16}$ inch in thickness. One would naturally suppose that solution would be directly proportional to the surface. If the rate of solution is not directly proportional to the surface exposed, then the test pieces would have to be of the same size, but furthermore, the results from

test pieces of any given size would not be applicable to pieces of other dimensions, which is a thing hardly to be thought of, and for present purposes the writer considers it fair to assume that the rate of solution is proportional to the surface exposed. This is not interpreted to mean, however, that the rate of corrosion transversed to the direction of rolling would be the same as in a parallel direction. The surfaces appeared most naturally to be equivalent surfaces in every respect. Large test pieces are more difficult to handle on account of the large quantities of acid required and they are also much more difficult to surface. On the other hand, the results obtained from them will doubtless be more accurate.

The Strength of Acids

Normal acids have been used in the experiments thus far and this appears to be suited to the work. However, stronger or weaker acids may be used if future results indicate the desirability of a change. The strength of acid should not be materially lowered during the course of an experiment and this can be accomplished by the use of relatively large volumes or by making the duration of the test as short as practicable. The small test pieces recommended by the Committee of the American Society for Testing Materials have a great advantage in relation to the volume of acid required over the test pieces used by the writer.

Temperature

A temperature of 16° C. has been chosen for the work thus far, but a somewhat higher temperature might be used if found desirable. It is sometimes difficult to keep the temperature down, especially when using nitric acid, and it becomes necessary at times to use large volumes of acid, a thermostat arrangement containing a coil through which a cooling fluid can be circulated, or to circulate the acid round and round through an external cooling device.

Kinds of Acid

The method depends upon the action of a non-oxidizing acid as compared to the action of an oxidizing acid upon the test sample of iron or steel. The two acids recommended are normal sulphuric for the non-oxidizing acid and normal nitric for the oxidizing acid. It

is true that sulphuric acid contains oxygen and that passivity can be induced by an electrolyte containing sulphuric acid under the influence of the current. Therefore, it is not strictly a non-oxidizing acid. However, its oxidizing effect does not appear to be of any consequence for the test work considered in the case of iron and steel and it is thought for various reasons to be more suitable than a halogen acid. Nitric acid is without doubt the most suitable oxidizing acid.

Weighing

The test plates are weighed before immersion in the acids and again after removal. They are taken out and washed rapidly with running water and dried. In the loss of weight are included not only the metal which goes into solution but also those substances which are disengaged from the metal complex and which remain attached to the surface, such as graphite, carbides, silicides, etc. Sometimes these can easily be removed by bristle or metal brush, but sometimes it is necessary, particularly in the case of cast iron, to sand blast the surfaces after the acid treatment, using great care not to cause additional losses of metal.

Calculation

Results may be reported as loss in grams per hour, per square centimeter or per square inch. Loss per square centimeter is preferable or this result may be multiplied by 10 or 100 if the operator so, prefers. By so doing the errors are multiplied but, on the other hand, fractional figures, which would otherwise be obtained for the purer irons in normal sulphuric acid, are avoided.

Index of Corrosion

The index of corrosion recommended represents:

1. The relation between the loss per square centimeter per hour in nitric acid and
2. The similar loss in sulphuric acid.

However, these figures must be retained, for purposes of interpretation, in their original magnitude. The index cannot be expressed as a simple ratio.

If we let O represent the loss per square centimeter per hour in normal nitric acid and H equal the similar loss in normal sulphuric

acid, then the index of corrosion, C, equals $\frac{O}{H}$. Index of corrosion, $C = \frac{\text{Loss per sq. cm. in normal } HNO_3}{\text{Loss per sq. cm. in normal } H_2SO_4}$. Unfortunately this expression does not permit of contraction or modification, at least, it has not been found practicable to simplify the expression with the very moderate amount of data at present collected. Two examples may be used to illustrate the point. The O index for a sample of very pure iron is found to be 12.0 and the H index for the same metal .05. Therefore Index $C = \frac{12.0}{0.05}$. A sample of gray cast iron is found to have an O index of 8.0 and an H index of 3.5. Therefore Index $C = \frac{8.0}{3.5}$. If these two ratios were expressed as single figures in the first instance, Index $C = \frac{12.0}{0.05}$ would become 240, and in the second case Index $C = \frac{8.0}{3.5}$ would become 2.3 (nearly). These figures are very far apart and it is considered advisable and recommended for the present to make use of the original data as obtained instead of attempting to express the index as one figure by dividing the H index into the O index.

Interpretation

In the first illustration given above, the rate of solution in normal sulphuric acid is very low and the rate of solution in normal nitric comparatively high. The interpretation of these data would be that corrosion in the absence of oxygen or with a limited supply of oxygen or air present, in this case would be low, but in the presence of an abundant supply of oxygen corrosion would go on relatively at a very rapid rate. The interpretation of the second case would be that corrosion under oxidizing conditions would be relatively low and much less than in the first instance, whereas corrosion in the absence of oxygen or when a relatively small amount was present would be comparatively very much greater than in the first instance. It should not be thought that the figures represent absolute ratios. Much more data would have to be accumulated and interpreted before any precise conclusions could be drawn, but since the rate of solution in non-oxidizing normal acid compared with the rate in normal oxi-

dizing acid appears to run parallel to the rates of corrosion when an abundant supply of oxygen is present and when a limited supply is present respectively, it is thought that a rational opinion of the corrodibility of a given kind of metal can be formed from its behavior in the two acids.

Thus the so-called index of corrosion presented here consists really of two indices which may be written together as a ratio for convenience but are subjects for separate consideration. In the examples cited, the H index for the sample of pure iron should be compared with the H index for the less pure cast iron and similarly the two O indices.

It is hoped that the suggested double index of corrosion for iron and steel will be applied by various workers to different samples of iron and steel whose rates of corrosion under different conditions are known and that in this way sufficient data will be accumulated to determine whether or not the rate of solution in non-oxidizing and oxidizing acids will serve as a measure of the corrodibility of a given sample of iron or steel.

DISCUSSION

President Wesson: Gentlemen, you have all heard Dr. Richardson's very interesting papers which throw a great deal of light on what has always been a more or less obscure subject, filled with many contradictions. Is there any discussion?

Mr. Badger: Mr. President, I don't feel competent to discuss Dr. Richardson's paper in general. It is too complicated to discuss on short notice, but one small question I would like to ask Dr. Richardson, not mentioned in the preprints; in the case of the cast iron samples were they as they came from the sand, or as they were machined?

Mr. Richardson: They were not machined. After these experiments they were machined, and I am experimenting on them now, but I am not inclined to take the view that the first surface had much or a very prolonged effect. It may have been active just at the start. I suppose you are speaking of the influence of possible silicon surfaces. I cannot give you the results at this time, but I do not think the sand surface was of much importance.

Mr. Badger: I have no evidence at all on the rusting of iron caused by the presence of a skin, but I have noticed the difference

in contact of various salt solutions in my evaporating machine, on those surfaces with that skin and those without it. In some cases there is a difference.

Dr. RICHARDSON: I don't think it would last long.

Mr. BADGER: The skin is a certain protection if you have corrosive agents not strong enough to take the skin, but which would take the polished surface.

Mr. RICHARDSON: After most of these experiments had gone for about one hundred days, all of the skin influence was lost and the whole surface was gone. That is indicated by the loss of weight shown in the tables. Therefore in all those cases wherein a considerable loss was sustained the skin influence was but transient and did not long persist.

Vice-President HOWARD: I wanted to say on that subject that it is a matter well known to acid manufacturers that castings not machined will resist the action of sulphuric acid or muriatic acid far better than when they are machined. The protective coating which you get from unscaled castings is a very real protection which lasts for a long time and gives very much increased life in the use of the commercial apparatus. I would like to ask if the brine mentioned here is simply a salt solution, or sea brine?

Mr. RICHARDSON: Ten per cent pure salt NaCl.

Vice-President HOWARD: I think it might be well to point out that the action is apparently quite different from the action of sea water, and the question of corrosion in sea water is of course one of great importance. Take, for instance, on page 261, the comparison of aluminum and copper. Judging by analogy, if we had no other experience, we would assume that the aluminum would be very excellent material for sheathing a ship's bottom, and that copper would be useless for that purpose on account of corrosion; whereas, as a matter of fact, exactly the opposite is the case, copper having been used for many, many years for that purpose, and lasting almost indefinitely, and aluminum as shown by the cup defender called the "Defender," built about 1895, actually rotted to pieces in two years' time, so that there was nothing left of the aluminum plates. I obtained some very interesting information regarding the corrosion of aluminum in sea water, from a United States Naval Constructor who is in charge of naval aviation construction work. He says that a sample of aluminum alloy which they got from a captured Zeppelin showed a remarkable tensile strength as com-

pared with ordinary aluminum. When the Aluminum Company of America attempted to duplicate this sample, by producing a product with the same analysis, the product which they obtained had nothing like the tensile strength of the sample and they then carried on heat treatment experiments extending over nearly a year, with the result that they finally succeeded in duplicating the German aluminum alloy and with also the surprising result that the heat-treated aluminum showed excellent resistance to corrosion by sea water, withstanding it almost perfectly for all practical purposes, in fact as well as an ordinary steel plate would on a ship.

This suggested to me while this paper was being read the possibility that heat treatment of steel might have a marked effect on its resistance to corrosion, and I wanted to ask Dr. Richardson if he had ever made any experiments on steel that had been so treated. If not, it would be interesting to carry out a series of experiments as to the effect of various heat treatments on the corrosion of steel and see if we cannot equal the extraordinary results obtained in the case of heat treated aluminum.

Mr. Richardson: I have not done anything on the heat treatment of steels but it affords a very interesting field, although in general its influence on corrosion has been overestimated. Nor have I experimented at all with sea water.

In reply to Mr. Howard I should like to say first that in order to interpret corrosion phenomena it is necessary to have at hand exact quantitative data as well as accurate observations. The literature of corrosion heretofore has been filled with the casual observations of engineers on the course of corrosion in machines, structures, water pipes, etc., unaccompanied by analyses or progressive quantitative data. Such observations while important cannot be given equal weight with the results of quantitative experiments under controlled conditions.

Answering Mr. Howard's points specifically, aluminum plates and particularly the older aluminum appear to be less homogeneous than copper plates as a rule and while aluminum plates show little loss by corrosion they do exhibit a greater tendency to pit especially near the edges than do copper plates under similar conditions.

On page 260 of the paper entitled "Experiments on the Corrosion of Iron and Steel," the description of aluminum and copper plates indicates this difference since the aluminum plates are described as exhibiting a few large pits near the edges whereas the copper

plates were coated uniformly with a thin tightly adhering layer of a malachite green color. This tightly adhering layer on the copper might well act after a certain length of time as a protective covering whereas the pits near the edges of the aluminum plates might result in early failure before a considerable quantity of metal was lost by corrosion. If the aluminum and copper plates used in the sheathing were painted in the cases cited by Mr. Howard, another factor enters into the case, namely, the relative adhesion and protection of the paint in the respective examples.

Sea-water is alkaline as shown by the reactions of various indicators and by the hydrogen ion determination. This alkalinity even though slight must be taken into consideration when comparing the corrosion of the metals, aluminum, iron and copper. The effect of an alkaline medium containing a large number of anions and cathions on aluminum might be especially pronounced and different from that on iron and copper.

Much has been said and written about the protective influence of the surface skin on cast iron. My opinion is that the effectiveness of this skin to protect against corrosion has been over-rated or over-stated but my own experiments are not final or conclusive on this point at the present time. However, that the surface skin is of importance I fully agree. Exact experimental data is needed to show just how important it is in corrosion under water and also when subjected to the action of acids in the chemical industry.

In connection with any discussion of the influence of the sand surface of cast iron against corrosion, attention should be directed also to the self-protective surface or auto-protective surface produced on metals by many corrosive acids and other chemicals. This is a more or less general phenomenon not only as regards metals but other materials of construction as well. The strong acid in contact with a metal frequently produces a surface or skin on the metal which is insoluble in the acid, thus protecting it against further action. The fire-brick lining of kilns is frequently protected by the formation of a protective skin of slag at its contact surface. Other examples will occur to anyone.

President Wesson: The points raised by Mr. Howard I think would lead us to suppose that the corrosion of steel is not altogether a question of chemistry, but largely a question of physics. In other words, the density of the metal would probably have a great deal

to do with its resistance. Is there any data to be furnished, Mr. Howard, regarding the specific gravity of the heated matter?

Mr. HOWARD: I have no detailed information regarding these results on aluminum. This information was obtained in a casual conversation, and accidental meeting with some gentlemen.

President WESSON: It is certainly a very interesting subject about which we want to know a great deal more than we do now.

THE MANUFACTURE OF LIME FOR CHEMICAL AND METALLURGICAL PURPOSES

By RICHARD K. MEADE

Read at the Montreal Meeting, June 29, 1920

Kilns employed for burning lime may be divided into two classes—(1) Intermittent and (2) Continuous Kilns. The latter class in turn may be subdivided into Rotary Kilns and Shaft Kilns. The shaft kilns may be again subdivided into Mixed-feed and Separate-feed kilns.

Intermittent Kilns

The intermittent kilns are usually known as "pot kilns" from their shape. (See Fig. 1.) They are primitive, uneconomical and are seldom used except for burning lime for the farm, where they are employed to some extent because they are inexpensive to construct as they can be built of rough local stone. These pot kilns are built in the side of a hill in order that the limestone may be dumped into the top by means of carts.

In charging such kilns, an arch of the larger pieces of limestone is first built 2 to 3 feet from the ground and the limestone to be burned is piled on top of this using pieces averaging in size from 2 to 8 inches thick. A wood fire is started below the arch and the flames from this pass up through openings in the latter and between the stone. The fire is usually maintained for about two days when the kiln is cooled. Old kilns of this sort are to be seen along the roads in any limestone country.

Continuous Shaft Kilns

As I have said, the continuous shaft kilns may be subdivided to two classes—mixed feed and separate feed kilns. Both types are used for producing chemical and metallurgical lime. In the former class, the fuel comes in contact with the limestone, in the latter, the fuel is burned on grates and only the products of combustion

come in contact with the limestone. The common type of mixed feed kiln employed by lime manufacturers is similar in design to a large pot kiln but is equipped with gates at the bottom of the kiln through which the lime may be drawn as burned.

Vertical kilns of mixed feed type used in chemical plants are very similar to the separate feed kilns described further on except that they are not provided with fire boxes on the side of the shaft. They consist generally of a shaft 40 to 50 feet high lined with fire brick and covered either with a steel jacket or with steel bands. They

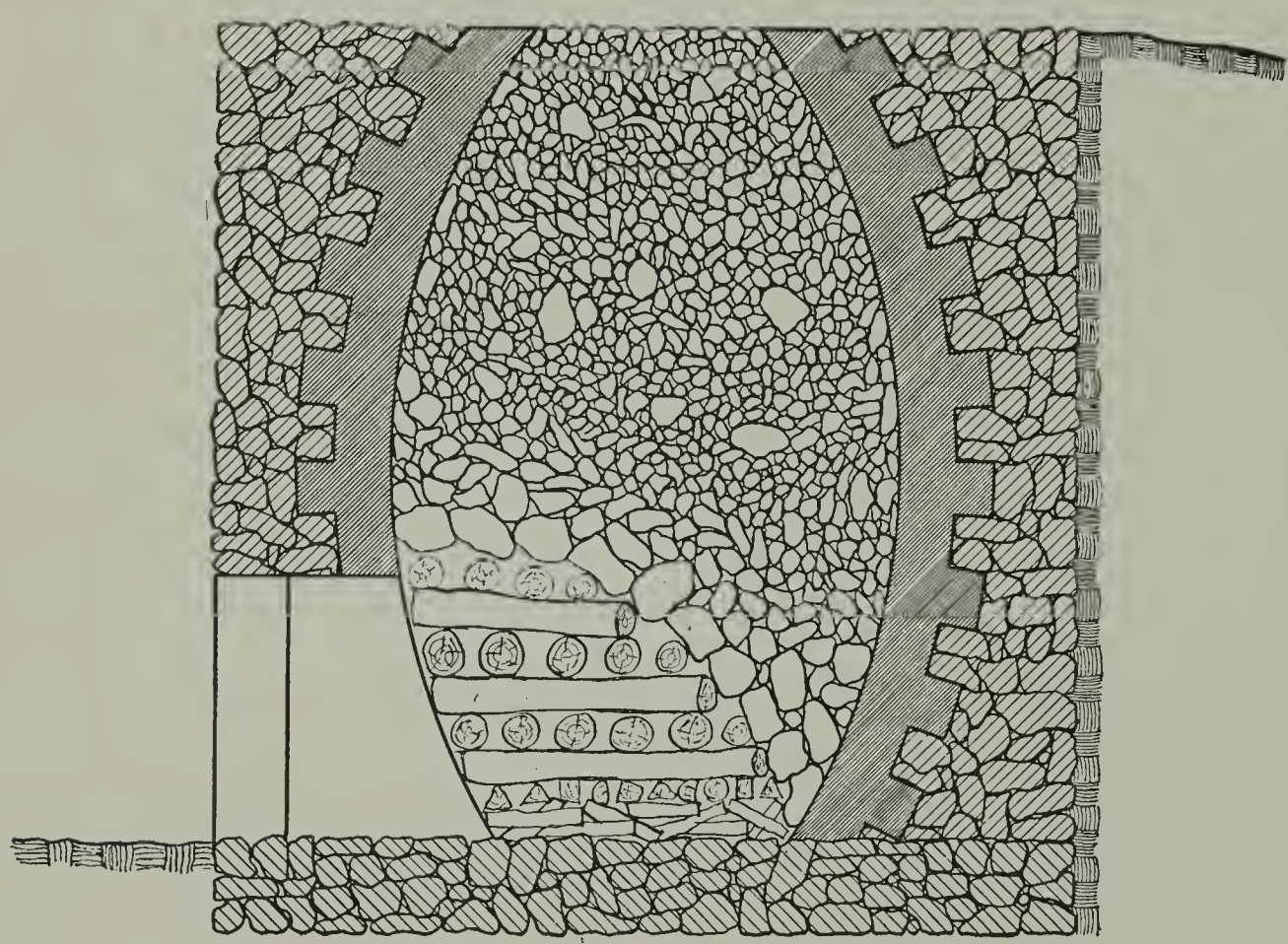

Fig. 1.—Old Style Pot Kiln.

are equipped with gates through which the lime may be drawn at regular intervals from below. When such kilns are used in the sugar and soda industries they are provided with a closed top and the products of combustion are drawn off by means of a fan in order that the carbon dioxide may be utilized. No detail description of such kilns need be given, as in a well-constructed mixed-feed kiln the structural features are quite similar to those described further on for separate feed kilns.

In charging such a kiln, the fuel (coke or small size anthracite coal) and limestone are added in alternate layers. Fire is started

at the bottom and works its way up. The process of charging and drawing the kilns is continuous. These kilns are economical of fuel and for the same size kiln give a larger quantity of product than do the vertical kilns with separate feed. Their exit gases are also usually somewhat richer in carbon dioxide. On the other hand, the lime is contaminated by the ash of the fuel. When such lime is used for building purposes or for metallurgical work, it must be carefully sorted in order to discard the lumps to which the fuel ash has adhered. Where the lime is to be slaked for milk of lime the separation of the ash and the lime can usually be effected by passing the milk through a screen or where used to causticize by placing the lime in a wire cloth basket and dipping in the causticizing tank.

Improved Shaft Kiln

The vertical kiln with separate feed usually consists of a steel cylinder lined with fire brick into the top of which the limestone is charged. The kiln is heated by from two to four Dutch ovens built into the side of this so that the products of combustion pass into the latter while the ash of the fuel remains on the grates. The burning is done in the zone between the ports of the furnaces. The lime is drawn out below.

Fig. 2 illustrates a shaft kiln designed by the writer, which may be taken as fairly representative of this type of kiln. There is nothing very original about the general design, but the lines have been so worked out as to give the proper fuel economy and quality of lime. Added to this are certain features intended to facilitate the operation of the kiln, cut down repairs, cheapen the construction, etc.

The dimensions of the kiln are altered usually to suit local conditions and the lime to be burned. With soft limestone, the kiln is not usually made so high as with the hard stone because the former will not stand so great a weight above without crumbling. Where the limestone is hard to burn, the diameter is usually less, while with easy burning material such as dolomite, the diameter is greater. The diameter is also increased where gas is used as fuel.

Generally speaking, the kiln consists of a steel shell 11 feet in diameter and about 38 feet high, which rests on a solid block of concrete and terminates in a steel cooling cone. This shell is divided into two parts. The upper 5 to 6 feet is unlined and forms a bin for the storage of the stone so that the kiln does not have to be con-

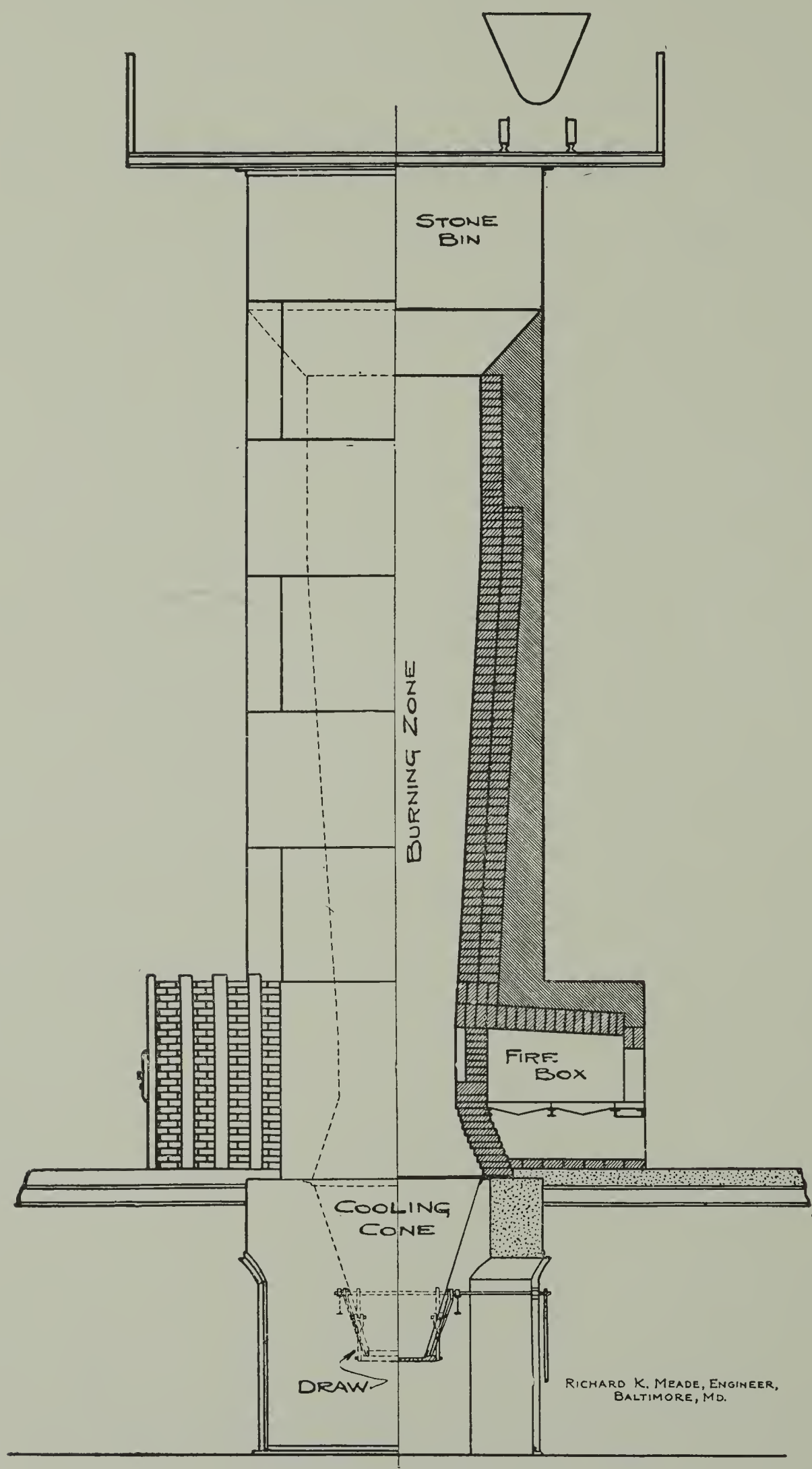

FIG. 2.—Vertical Lime Kiln.

tinuously charged. The lower section of about 32 feet is lined with fire brick and in this the stone is burned.

The kiln is equipped with two furnaces, one on each side. These are supported on a reinforced concrete floor level with the bottom of the shell and 12 feet above the floor on which the lime is drawn. Usually the reinforced concrete firing floor is extended from 10 feet. to 20 feet beyond the fire-box front in order to give ample space for the burners to work and on which to pile the coal for burning, etc.

The cooling cone is of steel plate and is so placed that the air can circulate freely around it. This cone receives the red-hot lime from the burning zone of the kiln. The function of the cone is to cool the lime. The bottom of the cone is closed by means of a pair of doors which swing from pivots supported by two small I-beams. The doors are pulled outward when the lime is to be discharged and pushed shut when this has taken place by means of a pair of levers. The cone is far enough from the floor to allow a car to be run under the doors into which the lime is discharged. The levers operating the doors are located outside of the kiln and permit the operator to stand away from the dust and heat while the lime is being drawn. The doors can be adjusted to give a close fit to the bottom of the cone. There is a free passage entirely around the cone and no blocking up occurs as in most other forms of discharge. The cone is provided with a poke hole closed by a sliding shutter to be used in case the lime does not discharge freely due, to arching. In some of the writer's newer kilns, he has placed a water-jacket around the upper part of the cone in order to increase the life of this.

The track by means of which the kilns are charged passes over one side of the kiln so that the cars dump directly into the center of the kiln giving an even distribution of the charge. The track is supported on light steel I-beams and a platform of perforated metal supported by brackets and enclosed by railings runs around the top of the kiln and between the rails. A heavy ring of steel plate protects the top of the brick from damage by the falling stone.

Where these kilns are used for building lime it is usual to carry the lime from them by means of barrows or cars. A more approved method, however, would be to place a pan conveyor under the cooling cone and draw the lime immediately on to this and so convey it to the point of use.

During the last few years the cost of the steel jacket for the kiln has been quite an item and a cheaper material which could be sub-

stituted for this has been desirable. Having great faith in reinforced concrete, this latter material naturally suggested itself to the writer.

As the result plans were drawn about three years ago for two kilns with reinforced concrete shells which were built at a small plant in Virginia. These have been in use for several years, long enough to show that the material and form of construction are entirely satisfactory. Since these were built the writer has designed reinforced concrete kilns for several other lime plants. There are other advantages in this form of construction besides cheapness, the principal ones being that the shells do not have to be painted as they are not subject to corrosion and there is less loss of heat by radiation.

The reinforced concrete kiln does not differ very materially from that which I have illustrated. Proper means are, of course, taken to heat-insulate the concrete shell. The cooling cone is made of steel and there is the same unlined top serving as a stone bin.

The arches over the furnace ports are a weak point in the shaft kiln. These arches are not only subject to destruction from the heat but they carry the weight of the lining, etc., above them. In the reinforced concrete kiln, this weight has been taken off of the arch by means of a reinforced concrete girder extending over the fire box.

With all types of shaft kiln one of the points to be watched is the draft. This must be so regulated by the design that the contents will be uniformly heated, otherwise some of the lime will be overburned and some of it not burned enough. In some instances, stacks are placed on the shaft in order to induce a better draft. Induced draft is also employed, the products of combustion being sucked from the top of the kiln by means of an exhauster. Where this is done it is, of course, necessary to close the top of the kiln and to charge the limestone into the latter through a door or a charging "bell" somewhat similar to that of a blast furnace. Fig. 3 shows such an arrangement. When the kiln gases are drawn off for their carbon dioxide this bell type is generally employed.

A less satisfactory method of artificial draft is to force the fire by means of a blast below the grates. This usually takes the form of a steam blower. If the fire is blown, there is a tendency for the flames to come out around the furnace door rather than to pass through the shaft but the steam itself is beneficial.

If the kilns are too large in diameter, the heat will usually not carry to their centers and so the stone in the center of the kiln will

not be burned properly. The writer has found that, owing to the fact that the gases from the fire box show a tendency to hug the sides of the kiln, the later may be made of greater diameter across the center line of the fire boxes than along this line. This makes a horizontal cross-section of the kiln at the fire boxes elliptical in shape. Two sides of the kiln are straight down to the cooling cone, while the other two sides are drawn in slightly as shown in Fig. 2. If drawn in too much, and with some stone if drawn in at all, the charge will stick and hang up in the kiln.

The lime is usually drawn every three to six hours, although a few plants draw oftener and some few less frequently. Large kilns are sometimes provided with a continuous draw. The objection to drawing too often is that each time the lime is drawn cold air enters the kiln through the drawing doors and cools off the charge. This same objection has been raised to kilns provided with a continuous draw, namely the continual current of air entering where the lime is drawn, passes up through the center of the kiln and prevents the proper burning of the lime at this point.

The charge sometimes sticks in the kiln and some openings closed by proper means are usually left on both sides of the shaft just above the furnaces through which bars may be introduced. It is claimed that kilns lined with silica brick show less "hanging up" than do kilns lined with ordinary fire brick due to the fact that the silica brick lining very soon scorifies and becomes smooth.

This type of kiln may be heated by wood, coal, oil, natural or producer gas. Wood is supposed to burn a better quality of lime than any other fuel, due to the low temperature of the flame and the length of this, and for this reason it is sometimes used for burning building lime; but it is very seldom used for burning chemical and metallurgical lime owing to its cost. The majority of kilns of the type given employ coal. This should be what is known as "long flame" coal, high in volatile matter and preferably low in sulphur and ash.

Where obtainable, oil makes an excellent fuel. When it is used in the kiln described, the burner is placed in the door openings of the fire boxes and these are bricked in with fire brick, leaving openings for the burner and for observing the lime, etc. The grate bars if already in place, are covered with fire brick, or, if a new kiln, the fire box is simply filled up to the point of the grate bars with some suitable material and covered with fire brick.

Natural gas may be used in this kiln and also producer gas but better results can be obtained by modifying the lines of the kiln to suit this latter fuel.

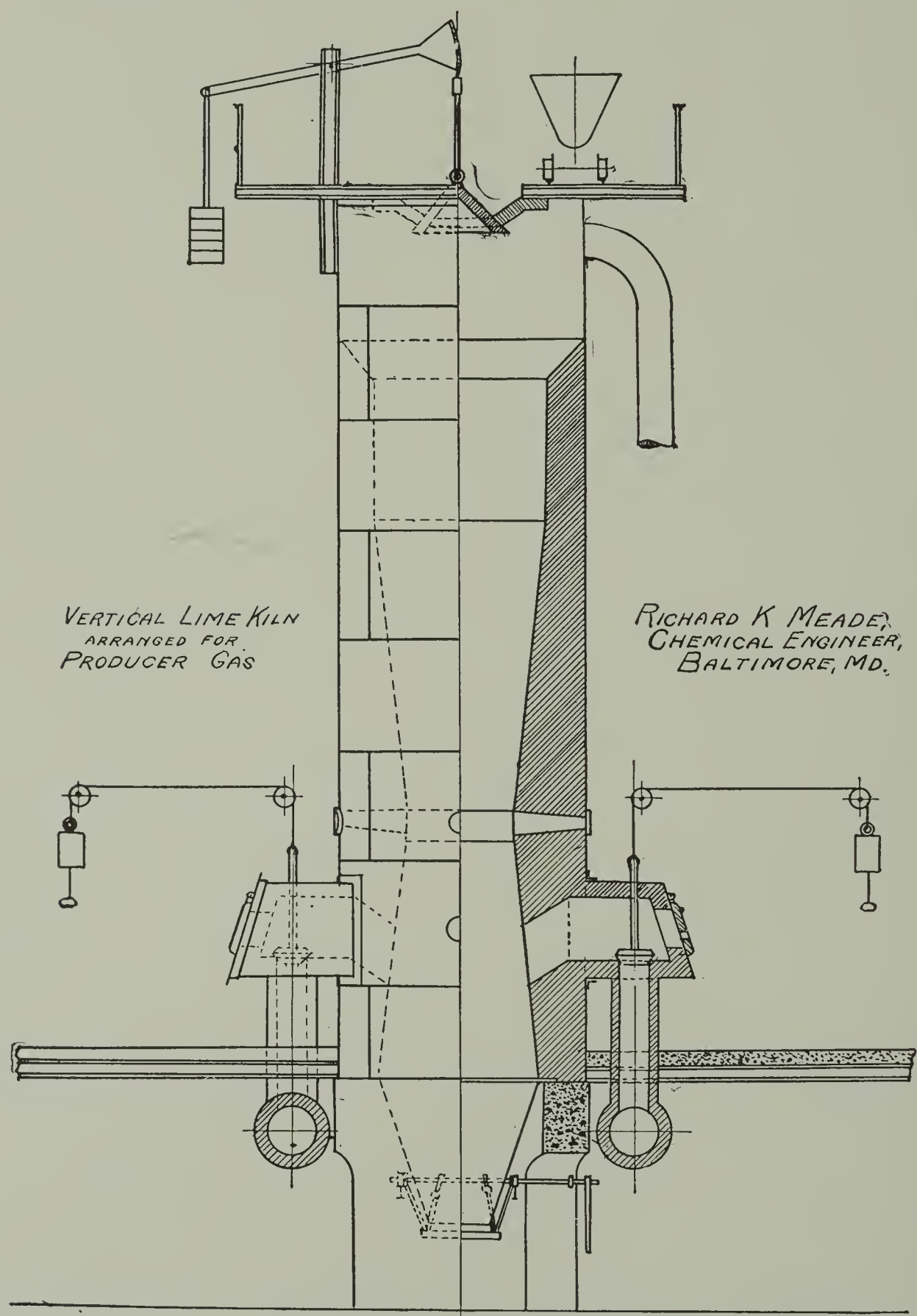

FIG. 3.—Vertical Fire Kiln Arranged for Producer Gas.

Producer gas is quite extensively employed for burning lime. Its advantages and disadvantages are a matter of dispute. One of

the principal good points is the fact that very much larger gas-fired kilns can be built than is possible with hand firing. Some of the more recent gas fired kilns have a capacity of from 40 to 60 tons of lime per day each. This increased size of the kiln is made possible by the introduction of gas and air at various points around the kiln so as to obtain uniform temperatures throughout the stack. Fig. 3 shows the kiln described above arranged for producer gas.

Producer gas kilns are slightly more economical of both fuel and labor than grate fired kilns. Unless carefully handled, however, they give lime which is unevenly burned. More skill is required in burning lime with producer gas than with any other fuel and considerable experimenting is usually done before satisfactory results are obtained.

In applying producer gas to vertical kilns, the main points to be watched are the proper mixing of the gas and air in the shaft and to prevent the accumulation of lime in the gas ports. This latter blocks the flow of gas causing irregular distribution of the heat and hence under-burning of the lime in certain parts of the shaft. In the type illustrated this trouble has been avoided by sloping the gas ducts downward towards the kiln. The points given further on in this article under producers for heating the rotary kiln follow also with the vertical.

The shaft kiln described heated with wood, coal or oil will produce from 8 to 12 tons per day depending on the kiln and quality of the limestone employed. When fired with gas the capacity will be from 17 to 25 tons.

The quantity of fuel required varies also and depends on many things, among which may be mentioned the kind and quality of fuel, skill of the operator and the limestone itself. Magnesian stone burns more easily than high calcium stone. The amount of fuel actually required is about as follows:

1 ton of good bituminous coal hand fired will burn from $3\frac{1}{2}$ to 4 tons of lime.
1 ton of good bituminous coal in the gas producer will burn from $3\frac{1}{2}$ to 5 tons of lime.
1 barrel of fuel oil will burn 1 to $1\frac{1}{4}$ tons of lime.
1 cord of seasoned hard wood will burn from $2\frac{1}{4}$ tons to $2\frac{3}{4}$ tons of lime.

The problem of carrying the stone to the top of the kilns is usually taken care of, where the kilns are located at the quarry, by means of a hoist and an incline, the latter running from the quarry floor to the top of the kiln. At chemical plants, where the stone is brought in by rail the incline may be used, or in many cases, a platform elevator is to be found more satisfactory because of the room saved.

A plan adopted at one of the plants designed by the writer would no doubt be satisfactory in many chemical works. In this plant the railroad cars are run on a trestle over storage bins. Each bin has an iron chute closed by a swinging gate through which the

Fig. 4.—Shaft Kilns—Four Completed and in Operation and Four under Construction.

stone is discharged. A track extends in front of the stone bins and 9 ft. below the bottom of them and the stone is discharged through the chutes into small side dump cars which are pushed along the track into the lime plant. The track is covered by a shed so that the drawing of the stone is not interrupted by bad weather. The cars after entering the kiln building are carried to the top of the kilns by a platform elevator.

Fig. 4 shows a battery of shaft kilns, and Figs. 5, 6, 7, and 8 details of this. Where only 8 to 20 tons of chemical lime are required one or two shaft kilns will prove the best plant, but where larger outputs of chemical lime are needed the rotary plant will prove more economical.

Rotary Kilns

The rotary kiln, which has been so universally adopted for cement plants, is now being employed to a growing extent for burning lime for chemical and metallurgical purposes. For burning lime to be so used it has many points of advantage over the shaft kiln, chief of

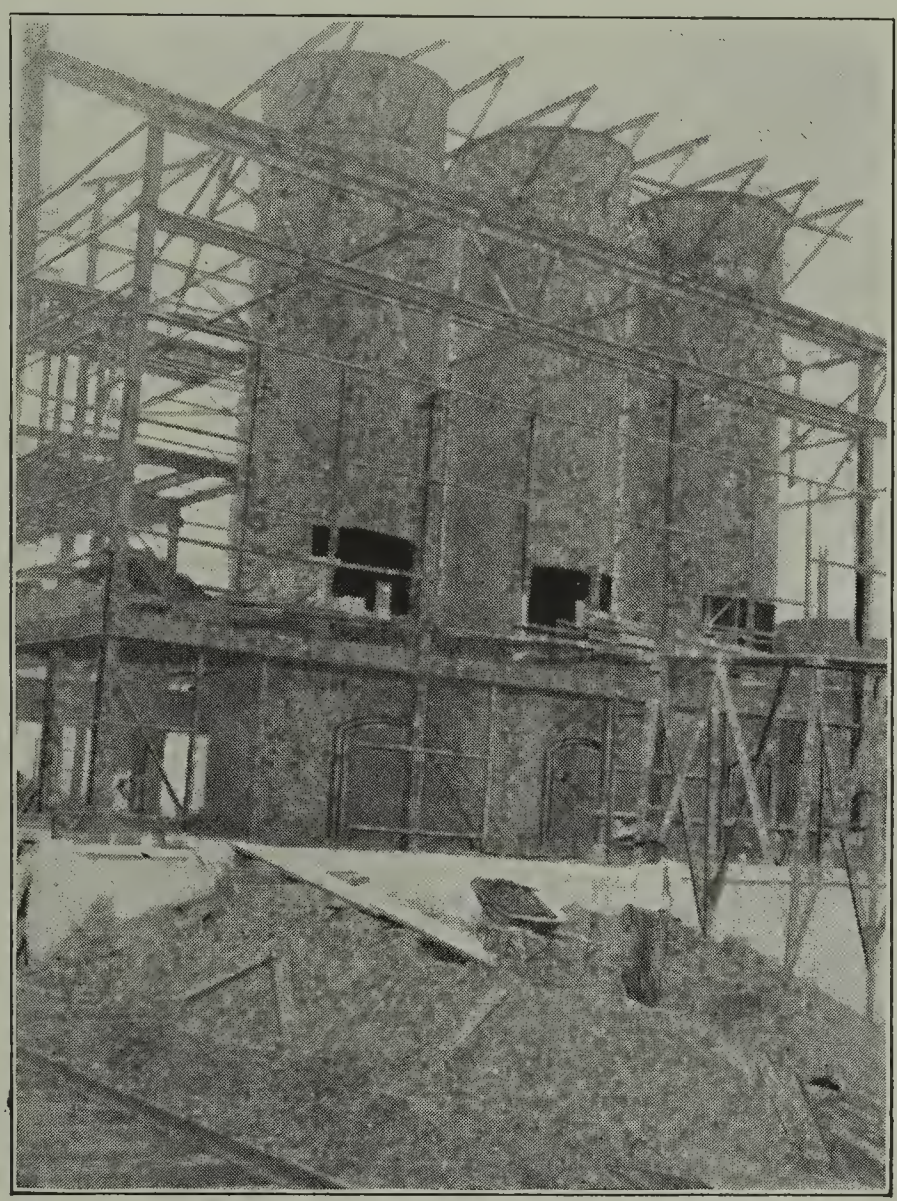

Fig. 5.—Steel Shells Ready for Fire-brick Lining.

which are the low labor and fuel cost of operating and the uniformity and thoroughness with which the lime may be burned.

There has always been considerable objection to the use of the rotary kiln for the production of building lime. This prejudice is to some degree due to ignorance on the part of the builder. Fine lime is generally the result of air slaking and as air-slaked lime is partly reverted to the carbonate, it is natural that the builder should demand lime in lumps. The product obtained by the rotary kiln

ranges in size from 2 inch to dust and is indeed often much finer than this. On being supplied with this fine lime, the builder supposes that it is air-slaked lime and refuses it.

At one or two plants producing rotary kiln lime, the lime is hydrated and sold to builders in the form of hydrate. The hydrate

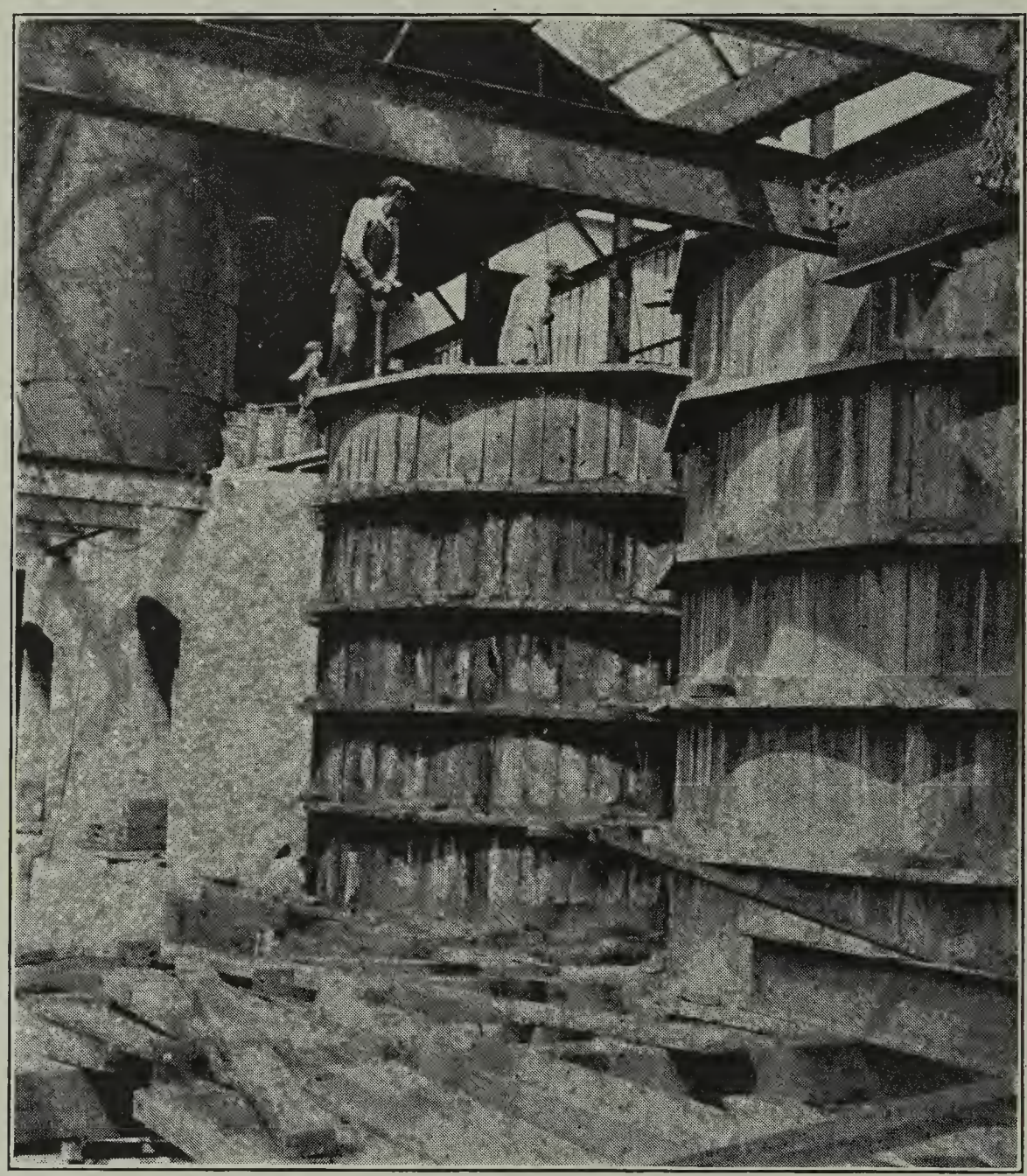

FIG. 6.—Concrete Pedestals under Construction. Movable Wooden Forms are Employed Here.

made from this lime differs very little, if any from that made from the ordinary grades of shaft kiln lime.

Where the lime is desired for chemical and metallurgical purposes such as in the manufacture of soda ash, wood pulp, carbide, cyanamid, calcium acetate, bleaching powder, bichromates, sugar, glass, ammonia, etc., for causticizing and furnace linings and flux—in short,

where lump lime is not necessary, the rotary kiln will prove superior to the shaft kiln provided the quantity of lime justifies the outlay.

The first definite proposal to use a rotary kiln for burning lime appeared in a patent which was granted to Henry Mathey of New York in 1885 (U. S. Patent No. 330,603) on a process of making lime which consisted in first crushing the stone to a suitable degree of fineness to pass a No. 4 or No. 6 mesh screen, then burning in a revolving furnace which he invented (U. S. Patent No. 325,259). This consisted of a rotary cylinder somewhat similar to the present-day kiln except that the center line of the kiln was horizontal, while

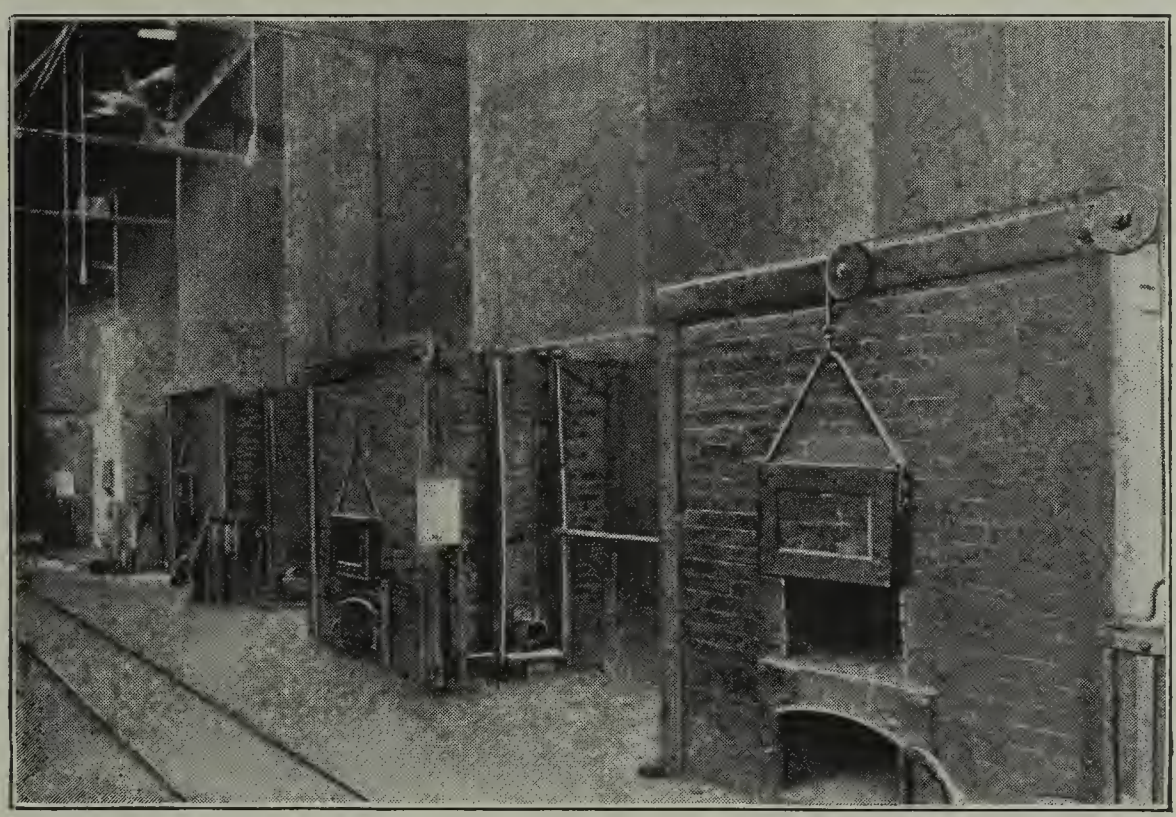

Fig. 7.—Fire Doors.

the kiln itself was made slightly cone shape, this latter serving just as does the inclination of the straight cylinder to work the material through as the furnace revolved.

The John G. Jones patent (U. S. No. 832,485) taken out in 1906, specifies the use of the present-day kiln but covers the burning of lime in a "granular condition with granules of such size as will readily pass a 1-inch mesh screen" and this phrase occurs in all his claims. In view of the fact, that you cannot patent the use of an apparatus and that Mathey had previously suggested the burning of limestone in a granular condition, it is difficult to see how Jones can sustain his patent.

Some experiments were also made in the early days of the cement industry on burning lime in rotary kilns. About 1905 the New York Lime Co. started to burn lime at Natural Bridge, N. Y. in a rotary kiln and shortly after this rotary lime kiln plants were built by both the Union Carbide Co. and the Aluminum Ore Co. There are now in operation quite a number of rotary kiln lime plants supplying lime for chemical and metallurgical purposes.

The Eastern Potash Co. are now installing at New Brunswick, N. J., a rotary kiln lime plant designed by the writer and equipped with ten rotary kilns, each 8×125 feet. This plant when completed will have a capacity of 1000 tons of lime per day and will be the largest lime plant in the world.

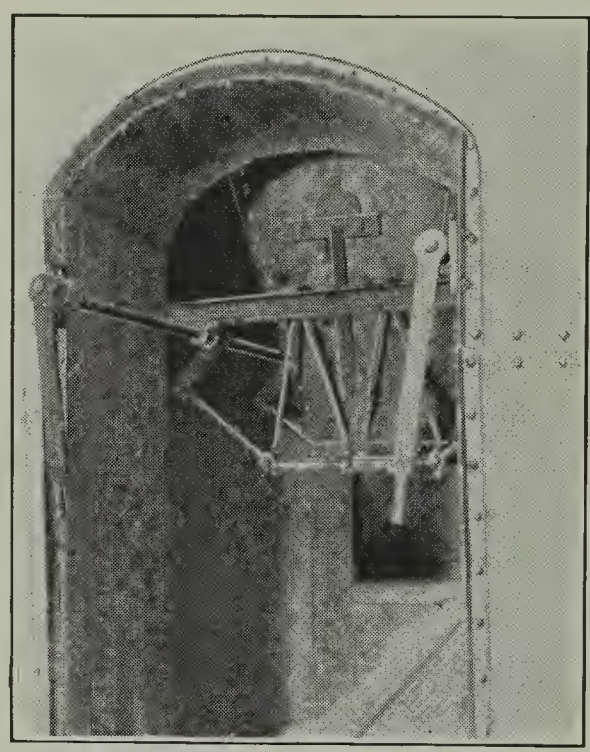

Fig. 8.—Cooling Cone and Swinging Door Draw.

The Air Nitrates Works at Muscle Shoals, Ala., is also equipped with a rotary kiln lime plant which contains seven kilns of the above size.

The Union Carbide Co. have two rotary kiln lime plants and no other kiln compares with the rotary one for burning lime for carbide because of the thoroughness with which this type of kiln burns the lime. Any unburned stone in lime for this purpose not only must be decomposed with a great expenditure of power in the electric furnace but the carbon dioxide liberated destroys the carbon electrodes.

The rotary kiln is now being quite extensively used also for burning dolomite for furnace lining. For this latter purpose much harder

burning is necessary than can be obtained easily in a shaft kiln. The rotary kiln is also pretty generally used for calcining magnesite in California.

The rotary kiln as used for burning lime does not differ in any particular from that used in the cement industry. It consists of an inclined cylinder from 6 to 8 feet in diameter and from 60 to 125 feet long. This cylinder is lined with fire brick and is supported on two or more steel tires which revolve on rollers. Power is received by means of a girt gear and supplied by a train of gears. The cylinder is slightly inclined from the horizontal, usually from $\frac{1}{2}$ to $\frac{3}{4}$ inch to the foot. The limestone is fed in at the upper end of the kiln and a jet of burning fuel is introduced at the lower. The limestone works its way through the furnace as the latter revolves and is burned by the gases passing through the latter, falling out at the lower end of the kiln.[1]

Fig. 9 illustrates a rotary kiln lime plant. The stone is held in a large bin and is fed from this automatically and continuously into the kiln. The latter is heated in this case by pulverized coal. The lime falls out of the kiln into a cooler with reduces its temperature to the point where it can be conveniently handled.

The capacity of various size kilns is given in the table below:

CAPACITY OF ROTARY KILNS BURNING LIME FROM LIMESTONE

Diameter, Unlined Shell, Feet.	Length of Shell, Feet.	Capacity per Day of 24 Hours. Tons.	Approximate Horse-power Required.*
5	60	18–20	4
6	60	25–30	5
6	100	40–50	$7\frac{1}{2}$
7	80	55–60	10
7	100	70–80	$12\frac{1}{2}$
8	125	90–100	17

* Motors should of course be larger, as this is actual average H.P. required.

The advantages of the rotary kiln begin with the quarry. With the old shaft kiln, whether of the most improved type or not, it is

[1] The construction of the kiln and its history and use in various industries was described in detail in the Transactions of the American Institute of Chemical Engineers, Vol. VII, p. 153, and in the Journal of Industrial and Engineering Chemistry of September, 1914, p. 754.

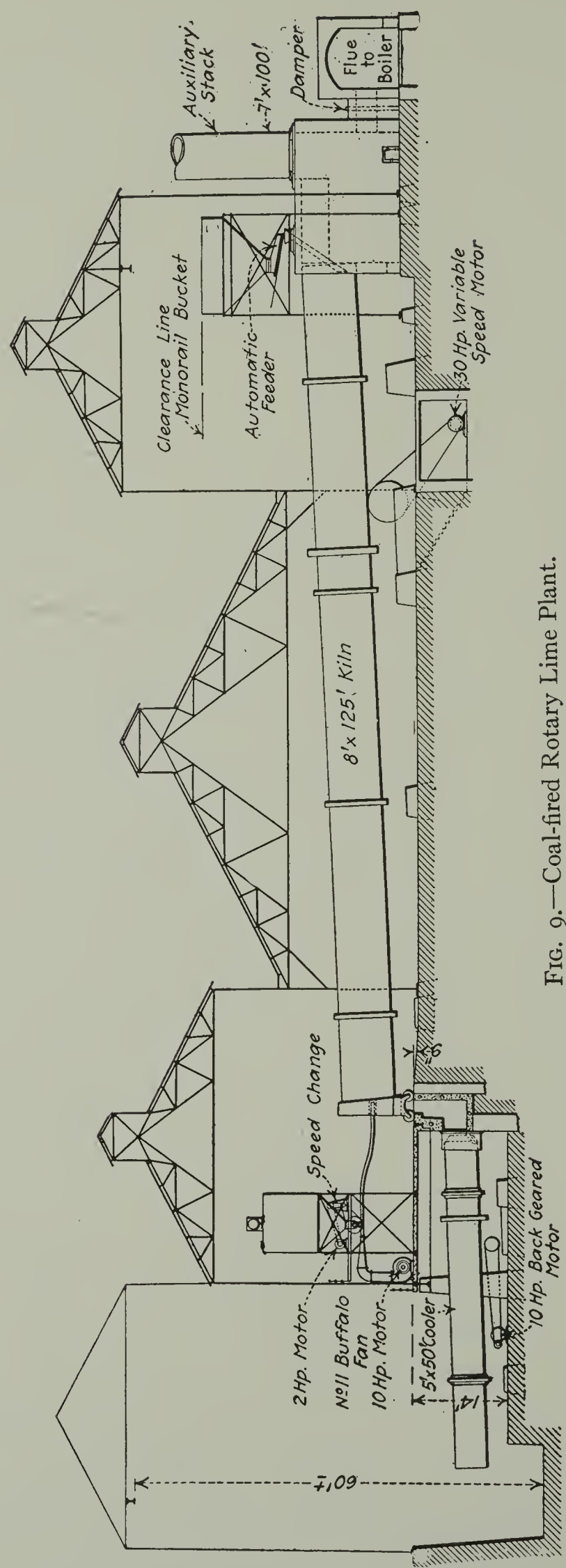

Fig. 9.—Coal-fired Rotary Lime Plant.

necessary to feed the kiln with stone of a certain size. If the stone is too big, the heat cannot penetrate to the center of the lump and consequently there will be a core or center of unburned limestone. If the stone is too small, the small pieces will work their way into the crevices between the larger stone and will choke the draft of the kiln, not only decreasing very materially the output of the latter but also causing irregular burning of the stone, due to the fact that the gases are forced to seek the path of least resistance and will probably avoid the central portion of the kiln in which the fine stone is more apt to lie.

As a general rule the stone for the shaft kiln should be brought down to a size ranging between 2 and 8 inches. Where the stone breaks up in the form of slabs, these latter can be quite long provided their least dimension is not greater than 8 inches.

The necessity of having the stone of this size increases very materially, not only the labor, but also the waste in the quarry. Where the small stone or spalls can be sent to a crushing plant or other use can be found for them, the item of waste is not so great but where they must be thrown away, the loss from this source is considerable. Quite a number of lime manufacturers have installed rotary kilns in connection with their vertical kilns with the express idea of burning up these small stones. The saving of labor in the quarry is very considerable. The sledging of the stone to proper size and the hand sorting and forking add much to the cost of this. Anyone with experience in such matters will appreciate the fact that stone can be crushed to 2 inches by a stone crusher much more cheaply than it can be to 8 inches by hand. "Cup grease" is much cheaper now than "elbow grease."

There are also numerous limestones which do not burn very satisfactorily in a shaft kiln owing to the fact that when the heat strikes them they decrepitate and fall into small pieces. In some cases, this action is very marked, the stone being almost reduced to dust. A very good example of this is the highly crystalline limestone found in the neighborhood of Franklin Furnace, N. J., some of the purest ledges of which have never been successfully burned in a shaft kiln due to this very action. Another limestone which is difficult to burn in a vertical kiln but which can be burned in a rotary kiln is the soft chalky limestone of Central Florida.

The saving effected in the quarry by a rotary kiln depends very largely on the size of the plant. If the plant is large enough, the

fact that the quarrying can be done with steam shovels will appeal to even the layman as a great saving over the process of carefully breaking down all stone to proper size by means of sledges [1] and then loading by hand on cars.

The earlier rotary kiln plants nearly all reduced their stone to quite fine material—passing the 1-inch screen or about $\frac{3}{4}$-inch and under. In the writer's opinion this is unnecessary and good results are now being obtained with stone crushed to pass a 2-inch screen. This has the advantage of saving power and simplifying the outfit required.

The power required to crush the limestone may be safely figured at about $1\frac{1}{4}$ H.P. hours per ton of limestone crushed which is equivalent to $2\frac{1}{2}$ H.P. hours per ton of lime produced (1.87 K.w.h.).

In small plants, which would naturally employ hand labor for quarrying, a small gyratory crusher with smooth concaves and head may be used, setting this to 2-inch, screening and returning the oversize to the crusher for recrushing.

As a general rule, better results can be obtained by screening out the dust from the coarse rock before burning. This increases somewhat the capacity of the kiln. This dust also contains a large part of the dirt which finds its way into the quarry so that the writer has found its removal is of advantage in increasing the purity of the lime. In localities where water is abundant, there would be no objection to washing the limestone to free it from dirt as the wet stone would not affect materially the operation of the kiln.

Probably most chemical manufacturers will purchase their stone. In which event, a good specification would be "to pass a screen with round perforations 2 inches in diameter and be retained on a screen with round perforations $\frac{1}{2}$ inch diameter."

If the stone is crushed by the chemical manufacturer, a slightly smaller dust screen may be used so as to reduce the quantity of material not burned. With a small gyratory set to 2 inches the fines will depend on the nature of the stone but will generally amount to about 10% of the stone crushed. A market can in most localities be found for this fine material as a road material or it may be still further pulverized and sold for fertilizers, asphalt filler, etc.

[1] If the shaft kiln plant is large enough to justify the cost of the installation of very large crushers, the steam shovel can be used here also and the limestone crushed in such crushers and sized by screens as is done by the Solvay Process Co., at Jamesville, N. Y. The waste in such a plant is large, however.

Where the limestone is purchased, it can either be dumped into bins from the cars as described previously or it can be handled in piles with a crane and a clam shell bucket. An excellent type of storage for the stone is the ordinary concrete silo. A silo 16 feet diameter by 40 feet high will hold about 30 cars of stone or sufficient for 200 tons of lime. The stone may be fed directly from such a small silo into one kiln by means of an automatic feed and a bucket elevator. If the storage is larger, however, or there are more than one kiln, it will probably be better to convey the stone as required from the silo to a bin above the kiln.

The feed bin for the kiln should be made of steel and preferably should hold at least twenty-four hours' supply of stone, unless there is also a silo storage when, of course, the bin could be very much smaller. Circumstances will indicate the storage required.

The stone may be fed out of the bin by any appropriate device. The writer has usually employed the ordinary reciprocating table feeder. This should be attached directly to the driving shaft of the kiln so that when the kiln stops revolving the stone ceases to feed. The feeder should be adjustable so that the rate can be regulated to suit the operation of the kiln.

The writer prefers to operate the kiln with a variable speed motor. This allows the operator, when the material is not being properly burned, to retard the speed of his kiln. This will cause the material to remain in the latter for a longer time and consequently will allow the heat to act on it to greater extent. When the material is burning well he can speed up his kiln, increasing the output, etc. In place of the variable speed motor, a speed change can be employed but this is less desirable.

The lime will leave the kiln at a temperature very close to 1800° F. It is, therefore, necessary in any large plant to cool the lime mechanically. This is done by dropping it into an inclined revolving cylinder through which a current of air is passed. Usually the air for cooling is drawn through the cylinder by natural draft. The cooler should be so arranged that the hot air will pass into the kiln and consequently the cooler will serve to preheat the air for combustion. A less desirable way of arranging the cooler is to provide it with its own stack, in which case, the advantage of the heat in the lime is lost.

In construction, the cooler is quite similar to a rotary kiln, except that in place of a brick lining, the inside of the cylinder has running through it Z bars or angle irons, which serve as lifters carrying the

material up and dropping it through the current of air passing through and so adding to the efficiency of the apparatus.

If desired, the cooler may be arranged with a proper device for slaking the lime also. In which event, it will probably be found desirable to provide it with a stack to carry off the steam rather than to allow the latter to enter the kiln.

I am giving below the approximate size cooler which will be required for various outputs of lime.

CAPACITY OF COOLERS

Diameter.	Length.	Capacity.	Approximate Horse-power Required.
3 feet	30 feet	$\frac{3}{4}$ to 1 ton of lime per hour	2
4 "	40 "	2 " $2\frac{1}{2}$ " " "	$2\frac{1}{2}$
4 "	50 "	3 " 4 " " "	$4\frac{1}{2}$
6 "	50 "	4 " 6 " " "	5

Pulverized coal, producer gas, natural gas and oil are all employed for heating the kiln. Localities where natural gas can be used are few and the cost of oil at the present time is prohibitive in most sections of the country, so that the fuels generally available are pulverized coal and producer gas. Natural gas is the most convenient fuel and producer gas the most troublesome. The fuel requirements of a rotary kiln are from 2800 to 3500 B.T.U. per pound of lime or

400 to 500 lbs. of coal per ton of lime;
37 to 45 gals. of oil per ton of lime;
500,000 to 625,000 cu. ft. of natural gas per ton of lime.

This is better than can be accomplished with the best hand-fired kilns and but slightly less than that claimed for the best types of gas-fired kilns. The quantity of fuel actually required depends just as in the case of shaft kilns upon the nature of the stone, the kind and quality of the fuel, the skill of the operator, and the kiln itself. The most economical kiln is one in which the ratio between length and diameter is greatest. That is to say, of two kilns having the same diameter but different lengths operated under the same condi-

tions, the longer kiln will have the greater fuel economy (and incidentally the greater output also).

Oil is a very convenient fuel to use and the installation also costs less, except where very large storage tanks have to be provided. When oil is used for a fuel, the apparatus necessary to heat the kiln is similar to that required for heating a boiler with this fuel. Almost any type of burner will work satisfactorily which will atomize the oil and give a conical flame. The writer has used Rockwell, Hauck and Kirkwood burners with success. He has also obtained equally good results with a burner which he had made up from his own design out of ordinary pipe and fittings. In all of his installations, he has employed air at from 30 to 40 pounds pressure for not only atomizing the oil but also for forcing it to the burners. In his system, there are in addition to the main storage tank, two small supply tanks, each of which will hold a supply of oil sufficient to last the kiln for from four to six hours and which are capable of withstanding a pressure of 100 to 125 pounds. The two tanks are used so that one will be in service while the other one is being filled. The oil is forced from these tanks to the burner by means of compress air, just as acids are lifted. The writer's experience has been that high pressure air atomizes the oil better than low pressure air and the use of air to force the oil to the burners does away with the oil pumps, and allows one apparatus to do the work of two.

Owing to the difficulty of securing oil cheaply in most localities, the average lime manufacturer, as I said, will have to decide the question of whether he will use pulverized coal or producer gas for heating the kiln. There are some points in favor of each. Producer gas will give the purest quality of lime. Pulverized coal on the other hand will be more economical and easier to handle.

Producer gas burns a nice clean lime. The temperature of the flame obtained is ample to burn good chemical lime and if the producer is a good one and is well taken care of, fairly uniformly burned lime, free from core, will be obtained. Producer gas, however, varies with the operation of the producer. The hand-fed hand-rabbled producers give a gas the quality of which depends very largely on the man who operates them. When such a producer is freshly charged with coal there is a rush of gas through the furnace. The gas then gradually decreases in calorific power until the next charge of coal is put in the producer. Automatically stoked and fed producers operate

much more smoothly and if at all well handled this objection is practically eliminated.

The producer should be located under a bunker so that the coal may be fed directly into the hopper of the former. Arrangements should also be made for removing the ashes conveniently. The producer should be located near the kiln so that no more heat will be lost by radiation than is absolutely necessary. The piping should be so arranged that the flues can be cleaned easily. Usually each kiln has its own producer or producers and no valves are inserted between the kiln and producer, the rate at which the producer is operated controlling the flow of gas to the kiln. Where two or more

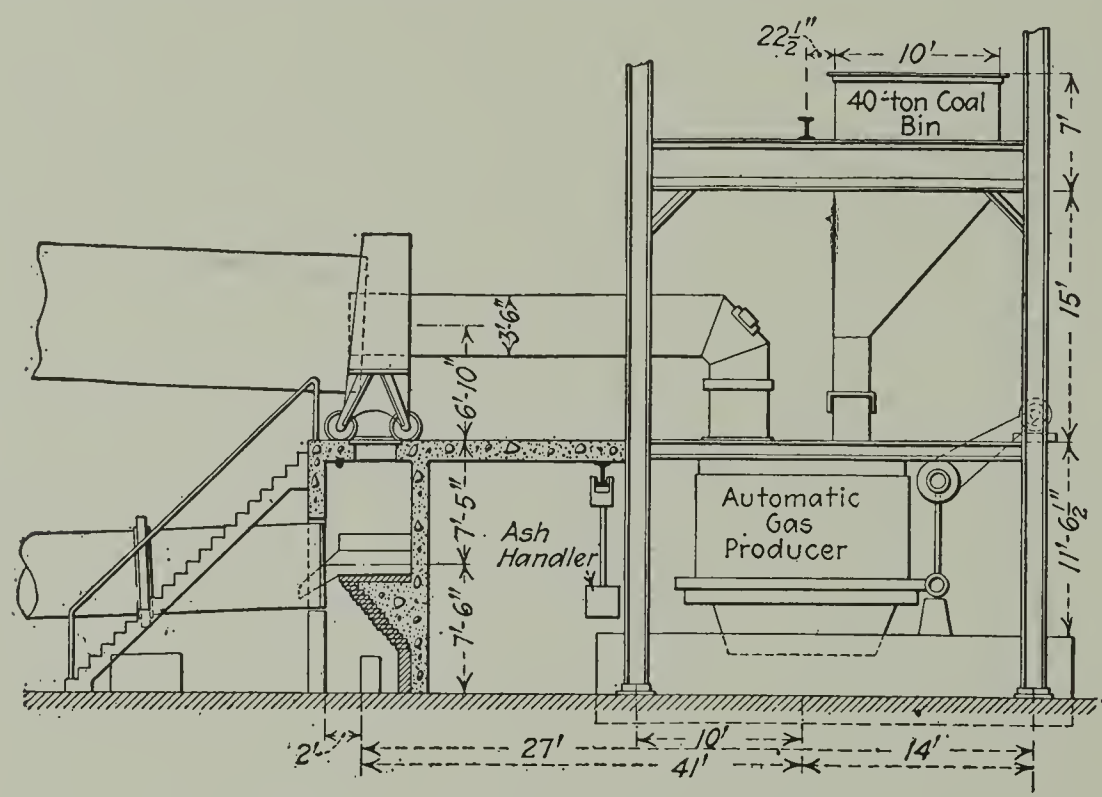

FIG. 10.—Producer Gas Installation.

small kilns, or where other furnaces also are heated from the one producer, etc., valves will, of course, be necessary. In the event a valve is not used, a sand damper or some means of shutting off entirely the producer from the kiln should be provided so that the lining of the latter may be repaired when desired without allowing the fire in the producer to go out, etc. Fig. 10 illustrates the installation of a gas producer in connection with a kiln.

As an 8×125-foot kiln will require from 20 to 25 tons of coal to heat it, or a gasification of about 2000 pounds of coal per hour, it will be seen that one kiln is large enough to have its own producer or producers and one large kiln is always to be preferred to several small ones.

The largest mechanically stoked producers will take care of from 3000 pounds to 3500 pounds of coal per hour or about 38 to 44 tons per day, but much smaller producers can be obtained with the automatic feed and stoking arrangement.

About 0.4 pound of steam will be required to operate the producer for each pound of coal gasified. This is equivalent to approximately one boiler horse-power per ton of coal gasified in twenty-four hours. Or an 8×125-foot kiln would require 20 to 25 boiler horse-power.

One man per shift can take care of a mechanically stoked producer with the help of another man part of one shift to get coal into the bunker, take away the ashes, etc.

I estimate the cost of producer gas in a well-equipped plant is approximately as follows, figuring on a producer which will gasify 2000 pounds hourly.

Attendants, 1 man at $4.00, 3 shifts	$12.00
" 1 " " 3.20, 1 shift	3.20
Steam, coal at $5.00	6.00
Supplies, repairs, etc	5.00
Cost per 24 tons of coal gasified	$26.20
Cost per ton	$ 1.09

Added to the above should be the losses from the producer. With smaller producers, cost of attendance would, of course, be more per ton, which would raise the cost of the gas.

The advantages which pulverized coal has over producer gas for heating rotary lime kilns are, first, the much more uniform rate of supply of fuel to the furnace, as where proper feeding devices are used there is a continual supply of fuel to the furnace at a regular and uniform rate and this fuel is, of course, of the same thermal value at all times and does not vary in this as does gas. Second, with powdered coal the loss of carbon due to that remaining in the ash is avoided. Third, it is possible to burn powdered coal with almost the exact quantity of air necessary for combustion which is not possible with producer gas. This means a higher flame temperature and a saving of fuel. Fourth, in the producer, there is a loss of coal due to carbon completely burned to carbon dioxide. A certain portion of this loss is of course conserved as sensible heat in the gas

and is utilized, provided the producer is set close enough to the kiln to cut down radiation losses.

The efficiency of a producer is seldom greater than 85% and is generally less than this compared with pulverized coal.

Experiments which the writer has made indicate that when pulverized coal is used about 40% of the ash of the fuel enters the lime. Assuming, therefore, that 450 pounds of coal are required to burn a ton of lime and that the ash amounts to 10% of the weight of the coal, one ton of lime would contain 18 pounds of ash or about 0.9%. I am giving below two analyses showing lime burned with pulverized coal containing 11% ash and what the same lime would be burned with producer gas.

COMPARISON OF LIME BURNED WITH PRODUCER GAS AND PULVERIZED COAL

	Analysis of Lime Burned With	
	Pulverized Coal.	Producer Gas.
Silica	2.44	2.10
Iron oxide and alumina	1.15	0.80
Lime	94.33	95.00
Magnesia	1.22	1.24
Loss on ignition	.86	0.86

A larger amount of ash will be retained by lime in which there is a lot of fine material, such as where the fine limestone dust has not been screened out, than will remain where the dust is screened from the coarse stone. The dust seems to catch and hold the ash rather than to allow it to be carried away by the draft of the kiln.

The cost of pulverizing 24 tons of coal daily is approximately as follows:

Drying the coal—0.2 ton coal at $5	$1.00
Attendants—1 man, 1 shift 8 hours at $4	4.00
Grinding 400 k.w.h. at 2 cents	8.00
Supplies, repairs, etc	4.00
Cost of pulverizing 24 tons	$17.00
Cost per ton	$0.71

It is hardly necessary in this paper to go into the various methods for pulverizing coal. The subject has been dwelt on quite extensively in technical literature the last few years.[1]

Sufficient to say, two general systems may be employed for heating the kiln with pulverized coal. One system in which the coal is pulverized and blown into the kiln at the same operation and the other in which the coal is pulverized in a separate plant, the pulverized coal conveyed into a bin at the kiln and fed from this into the burner as desired.

Fig. 11 shows the former installation in which an "Aero" pulverizer is used. This latter consists of a series of paddles which revolve

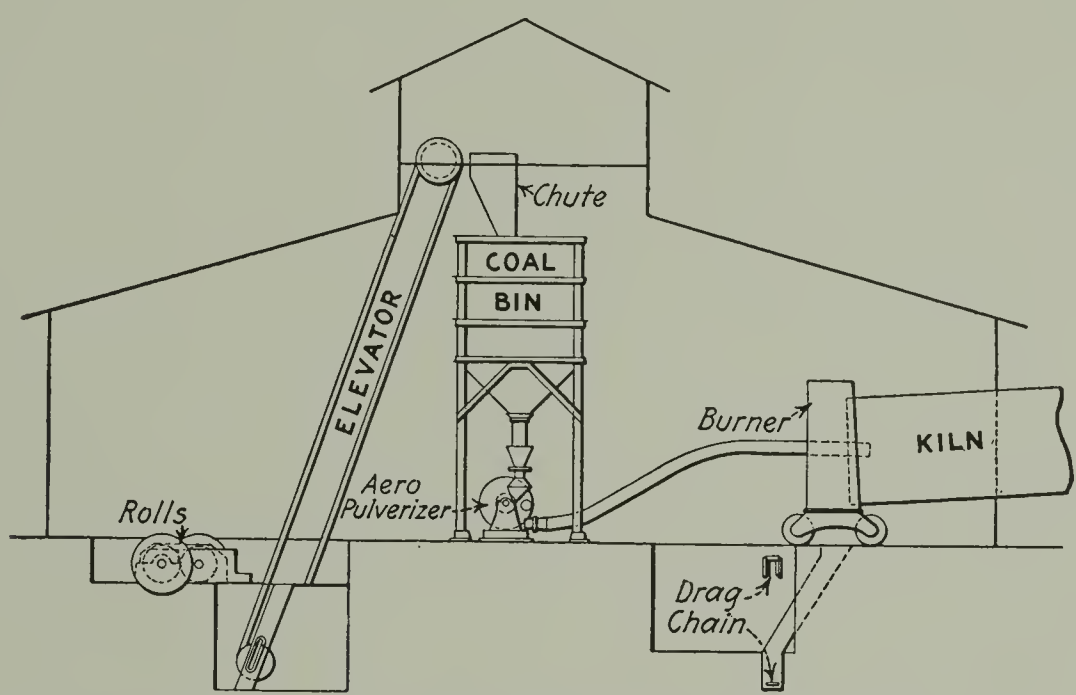

FIG. 11.—Rotary Kiln Heated by Aero Pulverizer.

about a horizontal axis in circular chambers through which air is drawn by means of a fan on the same shaft as the paddles. The coal is pulverized by being thrown against the walls of the chambers by the paddles and is drawn out with the necessary air for combustion and blown directly into the kiln through a pipe which extends directly from the pulverizer to the kiln. This pulverizer is supposed to work on damp coal and with Eastern coals has given fairly good satisfaction without drying the coal. With some of the coals in the Middle West, however, the experience has not been so good. The Aero requires about 18 H.P. hours ($13\frac{1}{2}$ k.w.h.) per 1000 pounds of coal pulverized or with ordinary fuel consumption about $7\frac{1}{4}$ H.P.

[1] See Meade, Transactions of American Institute of Chemical Engineers, Vol. I, p. 98.

hours ($5\frac{1}{2}$ k.w.h.) per ton of lime produced. It should be remembered in comparing this power with that required by other machines that the above includes power necessary to blow the coal into the kiln, etc. This machine may be looked upon as a cheap method of

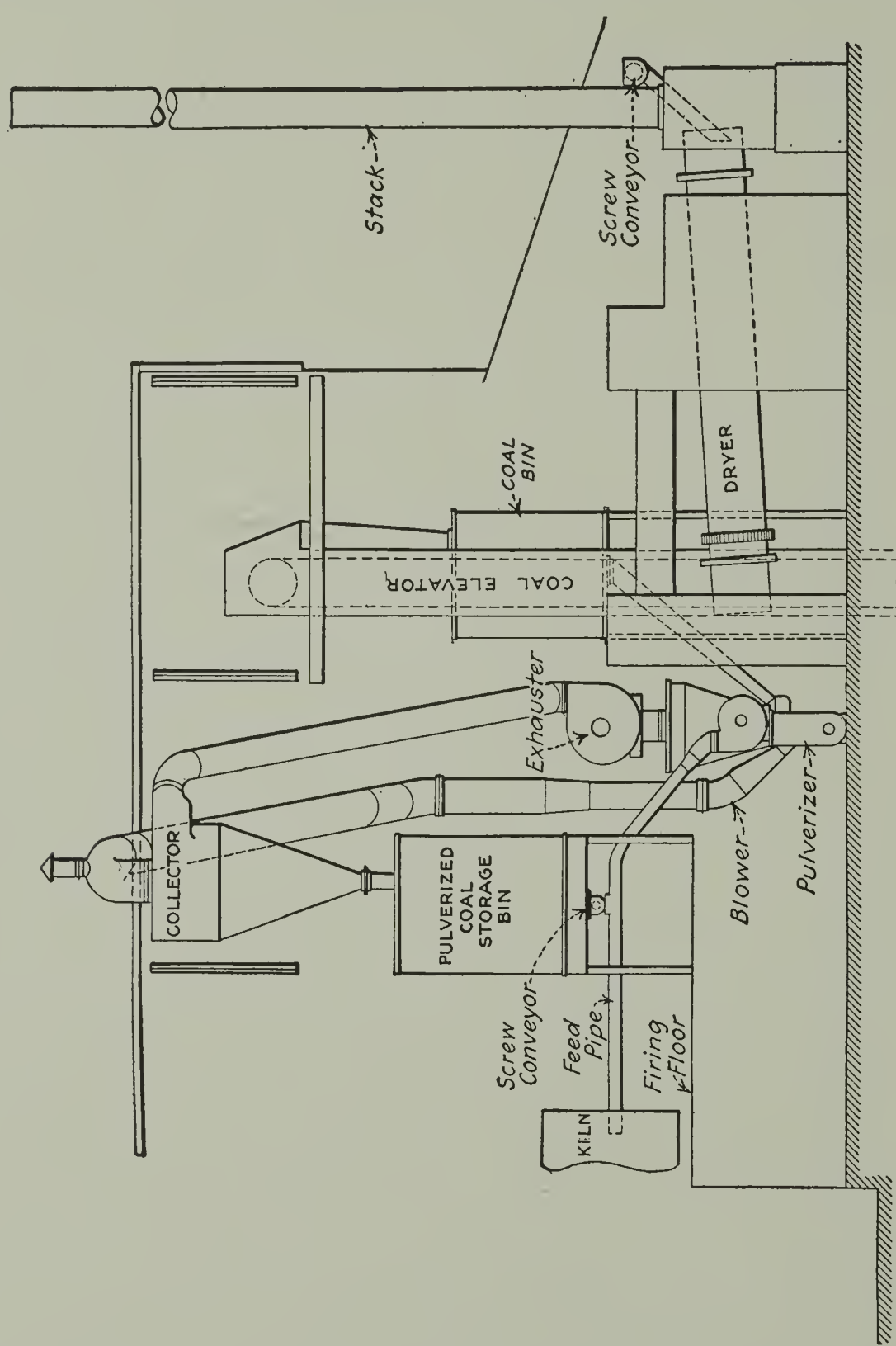

Fig. 12.—Rotary Kiln with Separate Coal Pulverizing Plant.

heating the kiln with pulverized coal rather than as the most efficient, as it does not pulverize the coal very finely.

The best method of preparing the coal and the one which would probably be used by a large lime plant would be to pulverize the coal

with either Raymond or Fuller mills and convey it into a suitable storage bin, from which it would be fed to the kiln as required. Fig. 12 illustrates this system, a Raymond mill being used.

Either one of these two pulverizers will require the coal to be crushed to about 1 inch and to have been dried. The Aero pulverizer will also require that the coal be reduced to 1 inch. For crushing the coal a set of rolls is usually employed and the drying may be done in any of the accepted types of rotary coal dryers.

The coal bin should hold sufficient coal to last the kiln sixteen to twenty-four hours so that the pulverized coal plant need not be operated more than one shift. The coal is fed out of the bin at a uniform rate by means of a worm, the speed of which can be altered to give the desired amount and dropped into the burner. Either steam or high or low pressure air may be employed to blow the coal into the furnace. Low pressure air at 6 to 10 ounces from an ordinary blower is usually employed, about 50% of that necessary for combustion being so supplied.

The waste gases leave the kiln at about 1300° F. and hence contain a large part of the heat liberated by the burning of the fuel. This heat can be successfully utilized in boilers as has been done in the cement industry [1] where an efficiency of 70% has been obtained. The weight of gases usually amounts to between 6500 and 7500 pounds per ton of lime produced. The heat in the same will, therefore, be approximately 2,275,000 B.T.U. This is about 40% of the total energy of the coal burned, the other 60% being distributed about as follows—decomposition of the limestone 54% radiation from the shell 6%. Of this waste heat 70% has been successfully utilized by waste heat boilers or about 3,500,000 B.T.U. per ton of lime produced. This is equivalent to 1550 pounds of steam at and from 212° F., or 45 boiler horse-power (hours). A kiln burning 4 tons of lime per hour, therefore, would be good for about 180 H.P. In the new lime plant of the Eastern Potash Corporation, designed by the writer, boilers are being installed. In most chemical plants where steam is needed for evaporation the plan should certainly be employed as not only power enough to operate the kiln can be obtained but considerable in excess.

If we deduct the fuel required to produce this power from that required to burn the lime, the efficiency of the rotary kiln will far

[1] See Baylor—Transactions of the American Institute of Chemical Engineers, Vol. X, p. 209.

exceed any other type. To produce 180 H.P. about 920 pounds of coal per hour will be required, while to heat the kilns 2000 pounds of coal per hour will be required leaving 1180 pounds of coal charged against the lime burning—or 7.4 pounds of lime per pound of coal.

Where the gases from the kiln are needed in the chemical process they can be drawn off from the kiln stack by means of a fan. Generally speaking the gases from a rotary kiln are not quite so rich in carbon dioxide as those from a vertical kiln due to the leak through the annular space where the kiln revolves in the stack chamber. By proper arrangements for closing up this opening as much as possible, a gas containing about 24% carbon dioxide on an average can be obtained. The waste gas always contains dust consisting of particles of limestone and lime and if pulverized coal has been used for burning the ash of this. The gases may be cleaned practically free from this by the use of water sprays, gas washers, etc.

The power required to operate a rotary kiln plant will be about as follows per ton of lime produced:

	H.P. Hours.	K.w.h.
To crush limestone	2.5	1.9
" revolve kiln, feeder, etc.	4.25	3.2
" " cooler	1.25	1.0
" pulverize coal separate plant	5.5	4.1
" feed and blow coal into kiln	2.00	1.5
" pulverize coal Aero system	8.00	6.0
Miscellaneous, stone elevator, etc	1.0	.8
Total where pulverized coal is used	16.5	12.5

One man can attend to the kiln provided the stone is placed in the feed bin for him. If there are more than one kiln, one man and one assistant can attend to as many as three kilns. If the Aero is employed to pulverize the coal, the kiln tender looks after this also. The coal, however, should be placed in the bin above this for him, so that all he has to do is to see to the proper operation of the kiln, cooler and pulverizer. Any good intelligent man can be broken in to operate the kiln.

Repairs to the kiln are light and consist in an occasional renewal of the lining at the lower 20 or 25 feet of the kiln. The lining of

the upper part of the kiln will last for many years but in the hottest part of the kiln the lining must be renewed every six to nine months, although a careless attendant can burn out a lining in a few weeks time. An allowance of 25 cents per ton will easily take care of repairs to the kiln, relining when necessary and the lubricants, provided the kiln is properly handled.

The cost of producing lime in a rotary kiln plant in the middle Eastern states is about as follows at this time. The first column represents cost with an output of 100 tons daily, stone quarried at the plant and a coal at $5 per ton. The second column represents cost with a 30-ton plant where stone is purchased and coal costs $7.50 per ton.

Stone, 2 tons	$1.50	to	$2.50
Coal, 0.2 ton	1.00	"	1.50
Labor	.20	"	.60
Power 15 kw.h. at 2 cents	.30	"	.45
Repairs, supplies, etc.	.25	"	.35
Total	$3.25	to	$5.40

Under existing conditions a rotary kiln lime plant of the best construction will cost approximately $950 per ton of lime produced per day. This figure includes a steel building entirely over the kiln and a pulverized coal plant or mechanically stirred producer. Where an Aero pulverizer or oil fuel is employed the cost is slightly less. It is not absolutely necessary to cover the whole kiln with a building which will also reduce the cost from the above.

Lime Recovery

An application of rotary kilns for burning lime of particular interest in the chemical industry is the employment of these for burning lime from the waste carbonate of lime, or "lime sludge," obtained from the manufacture of caustic soda by the action of lime on soda ash and in sugar refining. Large quantities of this waste are produced by paper pulp mills, caustic soda works and beet sugar manufacturers. The rotary kiln is now being employed for converting this waste into lime in all of these industries.

The attempts to burn the waste in a rotary kiln began about 1900 when the kiln was employed in connection with dryers. This com-

bination had already been tried on wet materials in the cement industry and proved a failure. The use of dryers in recovering waste was soon abandoned and the employment of long kilns, following the cement practice on wet materials, was substituted. This, in connection with various schemes for thickening the waste sludge so as to reduce the water to be evaporated have made the burning of lime waste commercially profitable.

The waste is usually received in the form of very thin sludge or slurry and it is necessary to dewater this by passing it through filter presses. The first presses employed were of the intermittent type. Recently, however, the continuous type presses have been found more satisfactory. The rotary presses are particularly convenient as the cake may be scraped from the latter directly into the kiln. As fed to the kiln under these conditions, the material usually contains from 45 to 55% water. It is desirable to reduce the quantity of water as far as possible in order to reduce the work of evaporating this in the kiln.

Generally, producer gas is used for burning lime sludge. Where available and cheap, however, natural gas or fuel oil would be superior fuels. Pulverized coal is not entirely satisfactory as the amount of ash introduced is quite considerable due to the much greater quantity of fuel required to burn the wet sludge. The wet sludge in the upper part of the kiln serves to catch and retain a large part of the ash which in burning limestone would pass out of the stack.

The capacity of a rotary kiln burning alkali waste will vary very largely with the water content of the waste when fed to the kiln. If properly installed a kiln burning lime waste will have about 60% of the capacity of the same kiln burning limestone—the actual amount depending to a large extent on how much water remains in the sludge.

The fuel requirements also vary with the amount of water in the sludge, but with a sludge containing 50% water the amount of coal required per ton of lime will be from 800 to 1000 pounds. The amount of natural gas will range between 11,000 and 14,000 cubic feet, while the oil will range between 72 to 90 gallons. The labor, power, repairs, etc., required to operate a lime recovery plant will be about the same as that required to operate a plant burning limestone with the addition of a man to watch the filter presses.

In many of the newer plants, mechanical filters are a part of the causticizing equipment and the operation of these would be con-

sidered as part of the causticizing plant. If possible, these filters should be located so that they can feed the cake directly into the kiln but where it is less convenient to do this the material can be carried from the press to the kiln on a belt conveyor.

Recovered lime consists of small slightly oval lumps ranging in size from that of a walnut down to dust. The color is slightly yellowish or greenish. The lumps slake quite a bit slower than rock lime and consequently causticize somewhat slower. On the other hand the resulting precipitated carbonate of lime usually settles much quicker. The lime will slake much more rapidly if the lumps are crushed before being added to the solutions to be causticized.

The lime will gradually pick up impurities from the process and also from the kiln lining so that it is not possible to burn the same sludge over and over indefinitely. Instead of starting with an entire fresh lot of lime, therefore, it is the general practice to introduce a small quantity of rock lime into the system at regular intervals and to sell a corresponding amount of recovered lime or discard the equivalent amount of sludge. This loss is usually made up by adding ground limestone to the kiln along with the lime sludge. The amount of lime necessary to replace losses usually amounts to about 5 to 10%. The recovered lime if burned at all skillfully will contain as much caustic lime as the best lump lime made from limestone. Lime sludge usually contains a certain small amount of caustic soda and the reburned lime of course contains this soda which is so recovered adding to the saving to be effected by the process.

The kiln used for recovering lime waste may also be used to burn lime from limestone provided the latter is crushed and there are suitable means at hand for feeding it to the kiln.

A lime recovery plant will cost approximately $1500 per ton of lime recovered. This figure includes filter press, gas producer and buildings.

BALTIMORE, MD.
June 21, 1920.

DISCUSSION

Vice-President HOWARD: Mr. Meade's paper is open for discussion.

Mr. MARSHALL: I would like to ask Mr. Meade the test of the carbon dioxide in the gas obtained.

Mr. MEADE: The exit gases contain about 33% of carbon

dioxide in the case of a shaft kiln and 28 to 30% in the case of a rotary kiln.

Mr. Marshall: I would also like to ask Mr. Meade whether dolomitic lime is burned more easily in the kiln than calcite.

Mr. Meade: Yes, it takes a little less heat.

Mr. Richter: By control with a pyrometer are the amounts of fuel reduced;

Mr. Meade: We have not found the pyrometer to be of much use in the control of rotary kilns. It is hard to install a thermocouple in a rotary kiln and the radiation pyrometers which we have used are so easily affected by dust, etc., that their readings do not seem to be trustworthy. The optical pyrometer is, of course, more accurate but is hard to use. We have found the automatic carbon dioxide recorder of value. If the percentage of carbon dioxide decreases, one can tell that the production of lime is falling off, because, the greater percentage of carbon dioxide in the kiln gases, the more lime is being produced. Similarly, when the kiln is drawn, if this operation lasts too long the cold air which enters at the gates will cool off the kiln. When the kiln is drawn the carbon dioxide in the kiln gases drops and the pyrometer will show the length of time during which the drawing lasts and gives a check on careless operation of the kiln in this particular.

Mr. Rhodes: You made the statement that pot kilns were not economical. The pot kiln is the first one devised and the most economical in point of labor and fuel consumption, up to the present time. It is used by one of the large steel companies for preparing lime for use in the open hearth and it is found to be very satisfactory for that purpose.

A pot kiln is charged during the daylight hours and is drawn down during four hours of the morning. Since the coke which is used for fuel is introduced into the kiln with the stone, it is not necessary to have any laborers on duty during the night hours while the kiln is burning the quantity of lime that is drawn the next morning. Coke is more expensive than coal but has greaer calorific power. When one considers this and the decreased amount of labor necessary, it is found that pot kiln lime can be manufactured more cheaply than any other class of lime. I do not recommend the use of pot kiln lime for all purposes. It is satisfactory for many metallurgical purposes and for agricultural lime, but is not suitable for building lime or lime for the chemical industry. It has been the history of

pot kiln lime that it could be purchased much cheaper than any other class of lime, and the reason lies mainly in the fact that its cost of production is low.

One feature of pot kiln lime burnt with low sulphur coke is that the lime is very low in sulphur. I made an extended investigation of this matter for the Blair Limestone Co. (Jones & Laughlin Steel Co.) and found that about 60% of the sulphur in the fuel is retained by the lime. Therefore, pot kilns using coke fuel are admirably adapted for producing lime for steel works.

Mr. Meade: Mr. Rhodes, when you speak of pot kilns, are you speaking of continuous draft kilns;

Mr. Rhodes: No, I am speaking of a kiln filled during the day and drawn during the following morning, in about four hours.

Mr. Meade: Oh, you don't let your fire die out entirely?

Mr. Rhodes: Oh, no.

Mr. Meade: I agree with you that such a kiln is economical, but I do not call that a pot kiln, but class it as a shaft kiln.

Mr. Rhodes: That is called a pot kiln in Virginia.

Mr. Meade: I think the term "pot kiln" should apply only to the small intermittent kilns and for those continuous kilns with drawing and charging arrangements and to one for a considerable height of stone the term "shaft kiln" is better and more scientific.

Mr. Rhodes: While Mr. Meade was reading his paper I thought of a refinement which I have never seen in any of the closed types of lime kilns. In the kilns employing the induced draft system, especially the larger size kilns, one finds that during the night time there is about 15 to 20% more production than during the day time. This is mainly due to the fact that during the hours of the day, the kiln is being loaded with stone and the hopper or door which closes the top of the kiln is being opened from time to time to allow the introduction of this stone. Naturally when the hopper is open the fan does not draw gas out of the kiln, but is wasting its efforts in circulating air drawn from the outside. I have often thought that kilns should be designed with a double hopper; i.e., a compartment in the top of the kiln having a door at the top and a door at the bottom, so that the stone might be dropped into this compartment and the top door closed, and then the bottom door could be opened and the stone discharged to the kiln. The amount of gas in this compartment would, of course, be very small and would be negligible in its effect. By this means one could get at

least 10% greater production out of the ordinary induced draft lime kiln.

I have found that the tendency in the last decade has been to design lime kilns of too great a size. I refer to the kilns having from 60 to 100 tons capacity in twenty-four hours. I have had experience with a battery of lime kilns designed to produce 60 tons of burnt lime in twenty-four hours and found that these kilns were exceedingly hard to manage. The area of these kilns at a section near the gas ports was very large. The kilns were 5 feet 6 inches across the fires and 15 feet from end to end. In drawing down a kiln of this size it is very difficult to poke them in such a way that the burden will fall solidly. There is a tendency for one part of the kiln to fall while the other part holds up, consequently the so-called "pitching effect" is often noticed. When a kiln gets in this condition it is difficult to produce good lime, for the reason that lime was mixed with stone in the fire zone and consequently the resulting product is both under-burned and over-burned. I believe that designers have gone too far in trying to produce these big units.

Mr. Meade: I agree with much that Mr. Rhodes says. The ordinary induced draft kiln has its top usually closed by means of a door which is opened and closed long enough to permit the dumping of a car of stone into the kiln, the operation often lasting a minute or two. The bell arrangement shown in Fig. 3 is designed to permit prompt opening and closing of the kiln. The operation here does not last more than a few seconds and the interruption of the draft is negligible.

The large gasified kilns do not seem to be entirely satisfactory. I only know of one operator who expresses entire satisfaction with them. I have found a gas-fired kiln producing from 20 to 30 tons of lime daily has proved most satisfactory.

Vice-President Howard: I would like to ask Mr. Rhodes what his experience was in consumption of producer gas compared with fuel burned directly.

Mr. Rhodes: Producer gas is the ideal fuel when burned in well-designed equipment. There is no question but that very high fuel economies can be achieved by the use of producer gas. Personally, I have seen kilns operated for extended periods with a fuel ratio of 6 pounds of lime to 1 pound of coal charged to the gas producer. It is very seldom, however, that such high efficiency is obtained, for the reason that many of the gas-producer plants have

been badly designed and are inefficiently operated. I have in mind one battery of kilns which is composed of approximately 35 kilns set in a row. There are two producers installed at the end of this battery of kilns and the gas is conveyed to all of the kilns in this battery through gas mains. These mains are not insulated in any way and the conduction and radiation is exceedingly high. By the time the gas reaches the last kiln in this battery it is comparatively cold and not nearly as active as the hot gas burned in No. 1 kiln of the battery. Consequently the production is much greater, in say, No. 1 kiln than in No. 35.

I have seen another plant in which the gas producer was condemned as a failure. I watched the operation of this producer one day and found that it was their regular practice to charge the producer with coal about once an hour. This, you can readily see, is extremely bad practice, for the reason that during part of the hour the producer is run very hot and a great portion of the carbon monoxide is undoubtedly oxidized to carbon dioxide. The best producer practice is to charge a gas producer lightly but very often. Before the day of the mechanical producers, one company found it very profitable to install four charging hoppers on top of their producer and to charge one of these hoppers every five minutes. A very good grade of gas was made in this way and its carbon dioxide content did not exceed 4%.

In comparison with gas producer practice, would say that the usualy good lime kiln using coal in the fire box produces about 4 pounds of lime per pound of coal charged. If one would take into consideration all of the lime kilns operating in the United States in which fuel is charged in fire boxes, it is my opinion that the average fuel efficiency would be 3 pounds of lime to 1 pound of coal used. There are, of course, notable exceptions. I know of one battery of direct fire lime kilns operating with the Eldred equipment which has a fuel ratio of 6 to 1. There are very few able engineers devoting themselves to the design and erection of lime kilns. Mr. Meade and one or two others are the only ones who solicit this kind of engineering work. It is my opinion that as time goes on lime manufacturers can be made to see that much of their equipment is obsolete and they will go in for the more efficient type of apparatus.

I have never seen rotary kilns operating with the efficiency that Mr. Meade describes. I have seen a number of the best-known installations of rotary kilns working on lime, but have never found

one that achieved a better fuel ration than 3 to 1. Of course the efficiency of the rotary kiln can be raised materially by the use of waste heat boilers, but as a general rule the temperature of the stack gases of rotary kilns is in the neighborhood of 1000° F., and the CO_2 content of the gas is about 12%. I do not think that these figures would point to a fuel economy as great as $4\frac{3}{4}$ to 1. Rotary kilns are usually used to burn quarry spalls and stone which fire spalls badly in a shaft kiln, but I do not think that the rotary kiln will ever supersede the shaft kiln for the burning of lime in this country. It does not seem to me to be economical to crush large-sized stone in mechanical crushers and grade it for use in the rotary kiln when larger pieces of stone can be burned in the shaft kiln without crushing.

There is one mistake that I have found very common in the design of rotary kiln plants. Many plants are not equipped with screening devices for the separation of the various sizes of stone and the necessary bins for storing this stone. If one would be successful in burning stone in a rotary kiln it should be graded into sizes such as, 1 inch, $\frac{3}{4}$ inch, $\frac{1}{2}$ inch, $\frac{3}{8}$ inch, etc. Very good results can be obtained if the stone is carefully graded and very low efficiencies have been obtained when the stone was not graded. I have in mind the plant which was erected by the Kelley Island Lime & Transport Co. This plant was designed to burn everything from $1\frac{3}{4}$-inch stone down to dust, but they soon found that this plan was not feasible and installed a screening plant to separate the stone into the various sizes. They then obtained excellent results.

Further progress in the art of manufacturing lime materials might be noted at this time. Prior to the World War manufacturers of open-hearth steel used to import into the United States large quantities of Austrian and Grecian magnesite. This magnesite was calcined and used for repairing the bottoms of open-hearth furnaces after holes began to appear in them. Even before the war, one manufacturer was accustomed to use hard-burned dolomite in place of magnesite. After the importations of magnesite were cut off, the demand for dead burned dolomite was exceedingly great and products made from it came into a great deal of prominence. At Kenova, W. Va., there was located a concern that calcined an impure dolomite containing a considerable percentage of iron, alumina and silica. This material was eagerly sought after and was found to be the best product obtainable on the market. J. E. Baker of York, Pa., also made a very fine product by double calcining dolomite, the last

calcination being conducted in a rotary kiln. It was found, however, that if dolomite stone were finely ground and mixed with a small amount of the flue dust or other iron containing material, this mixture would clinker at the highest temperatures obtainable in a rotary kiln, viz., 2300° to 2400° F. When once this clinker was obtained it was exceedingly difficult to melt it, and it was found that it made a very successful substitute for magnesite for use in the open-hearth furnace. Several new plants have been put up for the purpose of making this product and sufficient quantities will be available for the peace time production of steel made by the basic open-hearth process. Sometime ago I inquired from a number of the steel companies whether they intended to go back to magnesite, and they advised me that they had found the substitutes entirely satisfactory and did not believe there would be any call for Austrian magnesite in the future.

Mr. Meade: Mr. Rhodes says he finds the temperature of the gases from a rotary kiln to be no greater than 1000° F. I should like to call his attention to the fact that as usually installed there is a considerable leakage of air at the opening where the kiln enters the stack chamber and this lowers the temperature. By providing a proper seal here the excess air can be greatly cut off and the temperature of the gases raised. It is also possible to utilize gases at 1000° F. in waste heat boilers with good results although the higher temperature is desirable as a smaller boiler is required.

Mr. Rhodes thinks my figures for fuel required to burn lime in a rotary kiln are too low. I agree with him that most rotary kiln lime plants take more, but most such plants are poorly designed and as he says try and burn stone of all sizes at one time. Producers are generally operated very inefficiently due to lack of competent technical skill at the average lime plant. Pulverized coal or oil will give much better satisfaction and if the coal is good, one ton of coal (2240 pounds) should burn one ton (2000 pounds) of lime. In the cement industry the ratio is nearer one to six. The speed and pitch of the kiln, quality of coal, size of the stone, etc., all influence the fuel ratio as well as the operation of the kiln and producer.

Mr. Laib: Do I understand from Mr. Rhodes that in the rotary kiln practice manufacturers have found it advisable to screen all their products, and that they in turn burn these separate products under varying conditions?

Mr. Rhodes: Yes, it is now customary to size stone for calcin-

ation in the rotary kiln by a system of screens. These screens are usually of the flat pulsating type which are best suited for the classification of small-size stone. Each size is delivered to a separate bin and is separately calcined. There has been considerable difficulty in the burning of stone as large as 2 inches down to dust, and as I have previously stated it is now common practice to classify the stone very closely.

PROGRESS IN THE BYPRODUCT COKE INDUSTRY

Description of the Modern Practices and Methods Exemplified in the Ford Plant—Coke-Oven Gas—Market for Byproducts—Ammonium Sulphate—Light Oil and Gas Enrichment—Tar

By C. R. BELLAMY

Read at the Montreal Meeting, June 29, 1920

The year 1919 is memorable to the coke industry in the United States, for in it for the first time the production of byproduct coke exceeded that of beehive coke. This fact is at the same time of vital importance to all our industries. For as Floyd Parsons has expressed it, "The industrial prosperity of leading civilized nations depends upon their utilization of fuels and metals." In this statement is found the real significance of the change from beehive to byproduct coke predominance. Better utilization of coal, our basic fuel, is the beginning of real conservation.

Our byproduct coke-oven industry, with close to 11,000 ovens in operation at this time, is one of huge dimensions, and the modern coking plant is one of the great achievements of chemical and mechanical engineering. The results of a modern plant show what progress has been made. The high yields indicate improved methods, while the uniform yields indicate the extent in which operation is under control. A better knowledge of the factors that are essential for good results, coupled with the ability to control these conditions, is the feature of our best plants. Before going into details concerning operation data of one of the most modern plants let us briefly trace the growth of this industry and the progress that has kept pace with this growth. In the writer's opinion, the expansion of the byproduct coke-oven has been marked by three distinct periods, which, with the attributed cause are given in order of sequence:

1. Recognition by the steel industry that byproduct coke could be made that was superior to any beehive coke.

2. Recognition by the gas industry of the fact that in the by-

product coke oven was its opportunity for development on the lines of real efficiency and economy.

3. General conviction that the market for benzol, ammonia and tar was firmly established and able to absorb all possible production from coke ovens.

The first period was realized by overcoming the oldtime prejudice of the blast-furnace operator and then seeking his co-operation in determining what constituted a satisfactory metallurgical coke. To illustrate this, the work of the Semet-Solvay Co. in conjunction with that of different blast furnaces is most interesting. For years this company made daily all the tests of which it had knowledge, such as specific gravity, porosity, shatter, loss in CO, size of pieces and structure. These tests, accompanied by investigation and research at ovens and furnaces, finally led to the fixing of certain definite standards, and by strict adherence to these standards byproduct coke has come to sell at a premium. Factors which are considered essential to the production of high-grade furnace coke are:

1. Proper preparation of the coke in all respects, including size.

2. Uniformity of the coal mixture used in the manufacture of coke, thereby producing coke of reliable chemical composition.

3. Uniformity of heating of the charges in the oven, thereby controlling the physical structure of the coke.

Coke-oven Gas

The commercial value of the surplus gas from byproduct coke ovens was slow to be appreciated, and it was only about eight years ago that any general recognition of this value was apparent. Since then the progress in this direction has been so remarkable that to-day the byproduct oven looms up as the real solution to the problems confronting our public gas utilities. Very many of the large cities east of the Mississippi River are now supplied with coke-oven gas straight or mixed with water gas. The literature of the gas industry as concerns manufacture is now largely devoted to the byproduct oven and it has given us many valuable papers upon this subject.

In this field, again, co-operation has means success. Joint investigation by the two industries concerned has made it possible for the modern byproduct plant to deliver a coal gas that will pass the most exacting specifications as to B.T.U. candle-power and purity. And this gas can be produced so economically that no other process

can compete. Some of the factors that make the production of such high-grade gas possible are:

1. Proper mixture of proper coals.
2. Tight ovens.
3. Proper regulation of pressure in ovens and in the hydraulic mains.
4. Proper carbonization temperatures.
5. Constant and reliable observations.

Market for Byproducts

During the world war the byproducts from coke ovens were found to be indispensable. Because of their extensive application at that time the merits of these products are now appreciated to the extent that they are just as indispensable in times of peace. As soon as this market was established the coke and gas industry was quick to avail itself of the fact and the growth of the industry has been very rapid since then (1914).

The byproducts are the same now as before the war, although at that time the Semet-Solvay Co. was the only commercial producer of light oils. Improved methods have, however, resulted in much better yields of these products. This improvement consists chiefly in the control of operating conditions. There is an old coke-oven axiom, " Temperatures, incident to the so-called high-speed operation, seriously affect the yields." Under modern practice this has been changed so that it can be said that temperatures properly related to the speed of operation do not seriously affect the yields. And likewise the other determining factors are now under regulation.

The Ford Plant

The modern practices and methods are well exemplified by the plant of the Ford Motor Co. at River Rouge, Mich., which is considered by many to be the finest byproduct coke-oven plant in the world.

Early in May it was my good fortune to study this plant for several days, and in this article I want to discuss certain features of the equipment, operations and results which particularly impressed me. The data given here are those of actual results. The yields are especially important, not only because they are high but because of their uniformity through varying speeds of operation.

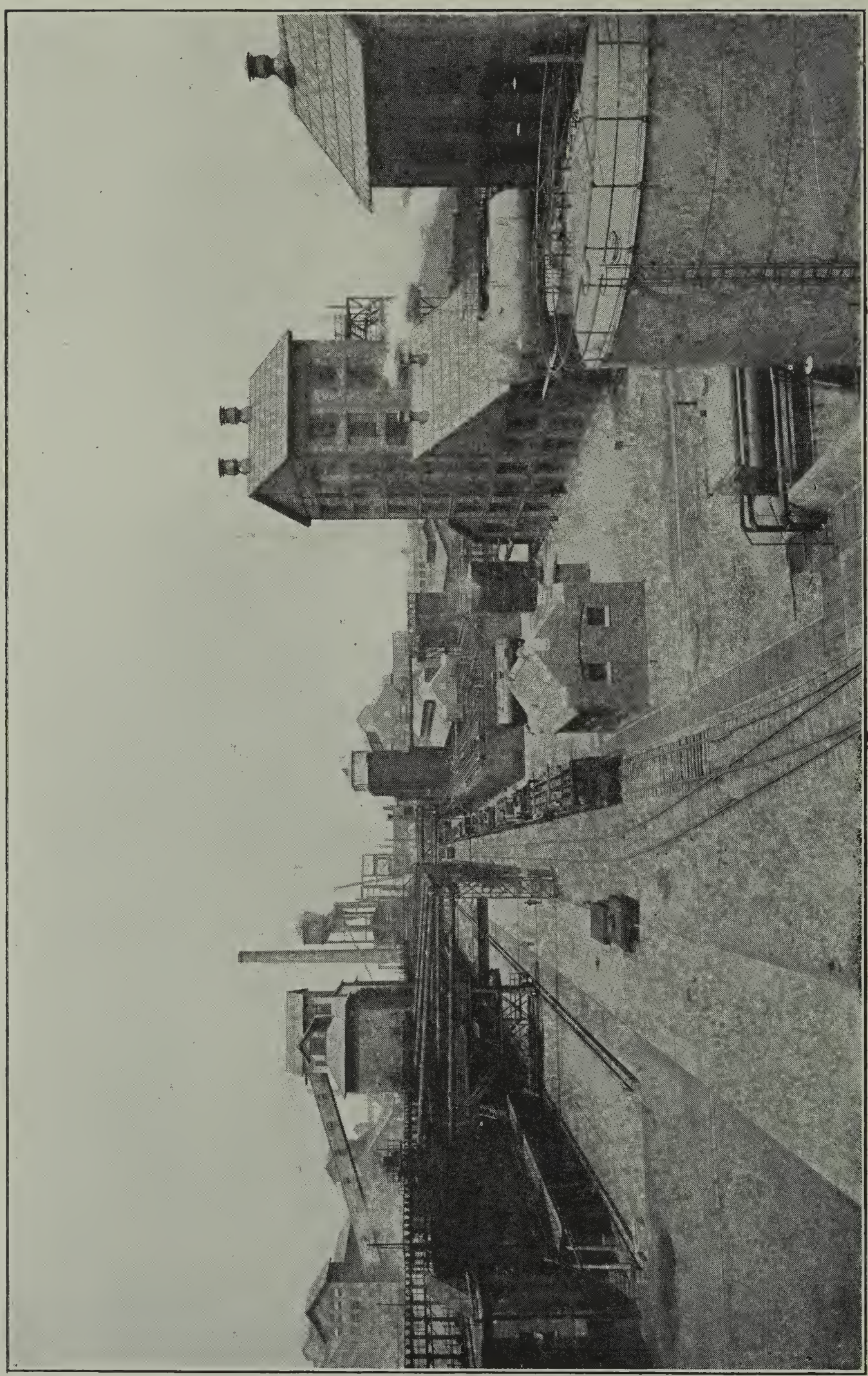

FIG. 1.—Pusher Side of Ovens with Light Oil and Benzol Plants in Foreground at Right.

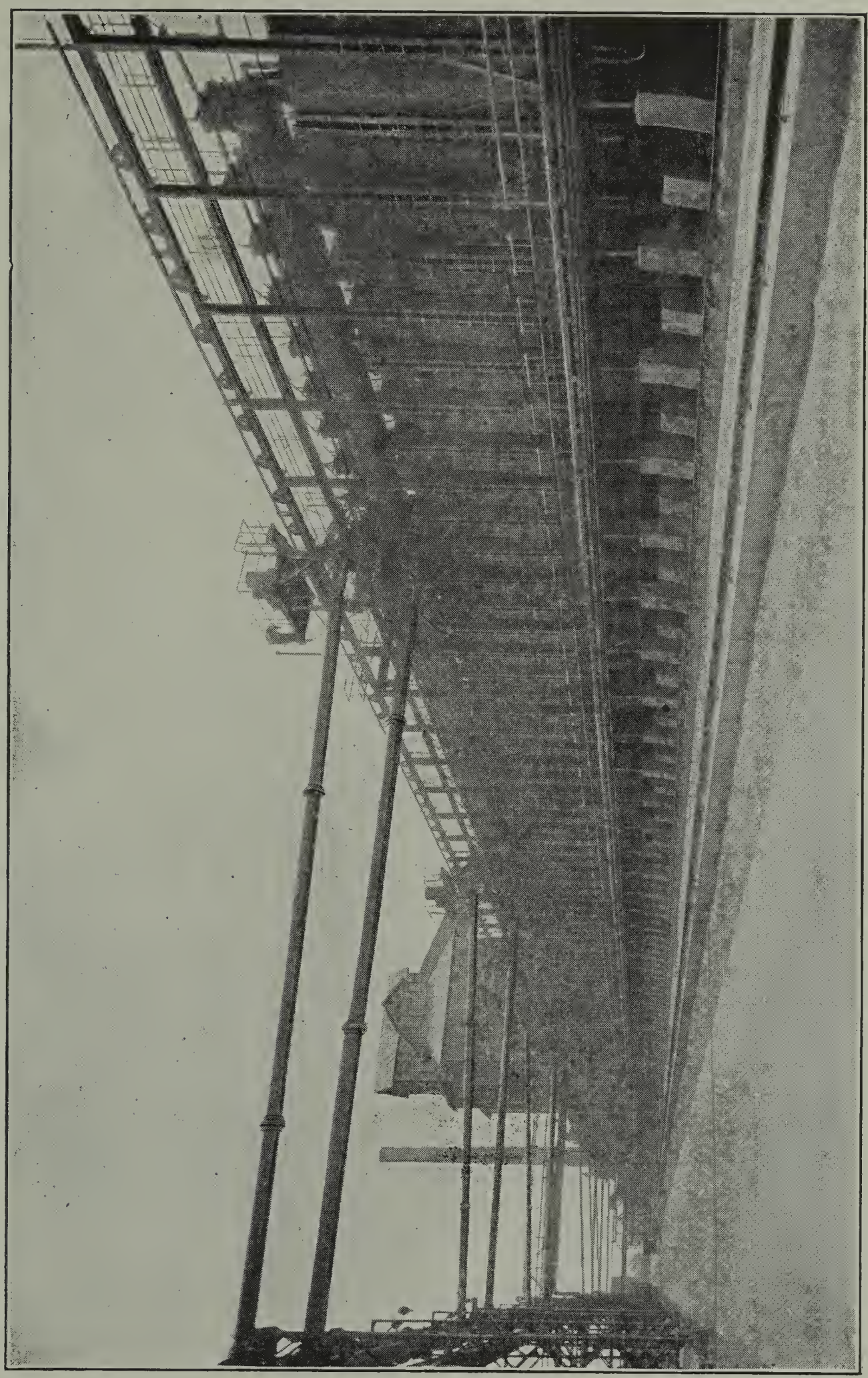

FIG. 2.—Pusher Side of Ovens.

This plant was completed and put in operation in October, 1919. Its chief function is to supply a high-grade metallurgical coke to the Ford blast furnaces. At the same time a contract with the Detroit City Gas Co. calls for 10,000,000 cubic feet of 18 candle-power and 600 B.T.U. gas per day. Thus these ovens constitute a combined coke and gas plant and must maintain the highest quality in both products. To do this the speed of operation must not give rise to conflicting factors, but rather all conditions must be properly co-ordinated to the speed of operation. Due to the unsettled conditions in the coal and railroad industries this plant has not had any really fast operation. In fact, very few plants have operated at full capacity during the period under discussion. The operation, however, has been performed at somewhat varying speeds, so that a study can be made of the effects, if any of such changes.

The Ford plant consists of 120 standard Semet-Solvay regenerator coke ovens, built in two batteries of equal size. Each battery is independent of the other in regard to control of operation. The gas direct from the ovens is received by a double hydraulic main, one main taking the rich gas given off during the first period of carbonization, while the second main receives the remaining heavy gas. This separation of gas during carbonization is performed in the usual manner—that is, by valves which are easy to open and close and which can be reversed when and as often as desired. The rich gas and lean gas are treated exactly alike up to the benzol scrubbers. Here the treatment is different and after passing through these scrubbers the two gases travel different paths, the lean returning to the ovens, the rich gas after enrichment and purification going to the city. The apparatus and equipment used to handle the gas is built in triplicate, one unit for the rich gas, one for the lean, with the third and middle unit as a spare. This spare unit is so connected to the system that it can take care of either the rich or lean gas as necessary. The importance of this feature is that repairs, apparatus cleaning and inspection do not cause inefficient or irregular operation. Having a spare system of byproduct recovery apparatus and a spare for all essential machinery used on the ovens, this plant is enabled to operate on a timetable schedule. Every oven is pushed at the exact time scheduled, the schedule being observed with railroad precision. This regularity of operation which is essential to the production of a satisfactory quality of surplus gas, where high standards are required, means also that the load on byproduct apparatus is uniform and

favorable for maximum byproduct yields. In the table of results it will be noted that the initial rich gas has been produced without an appreciable variation in B.T.U. value for over three months.

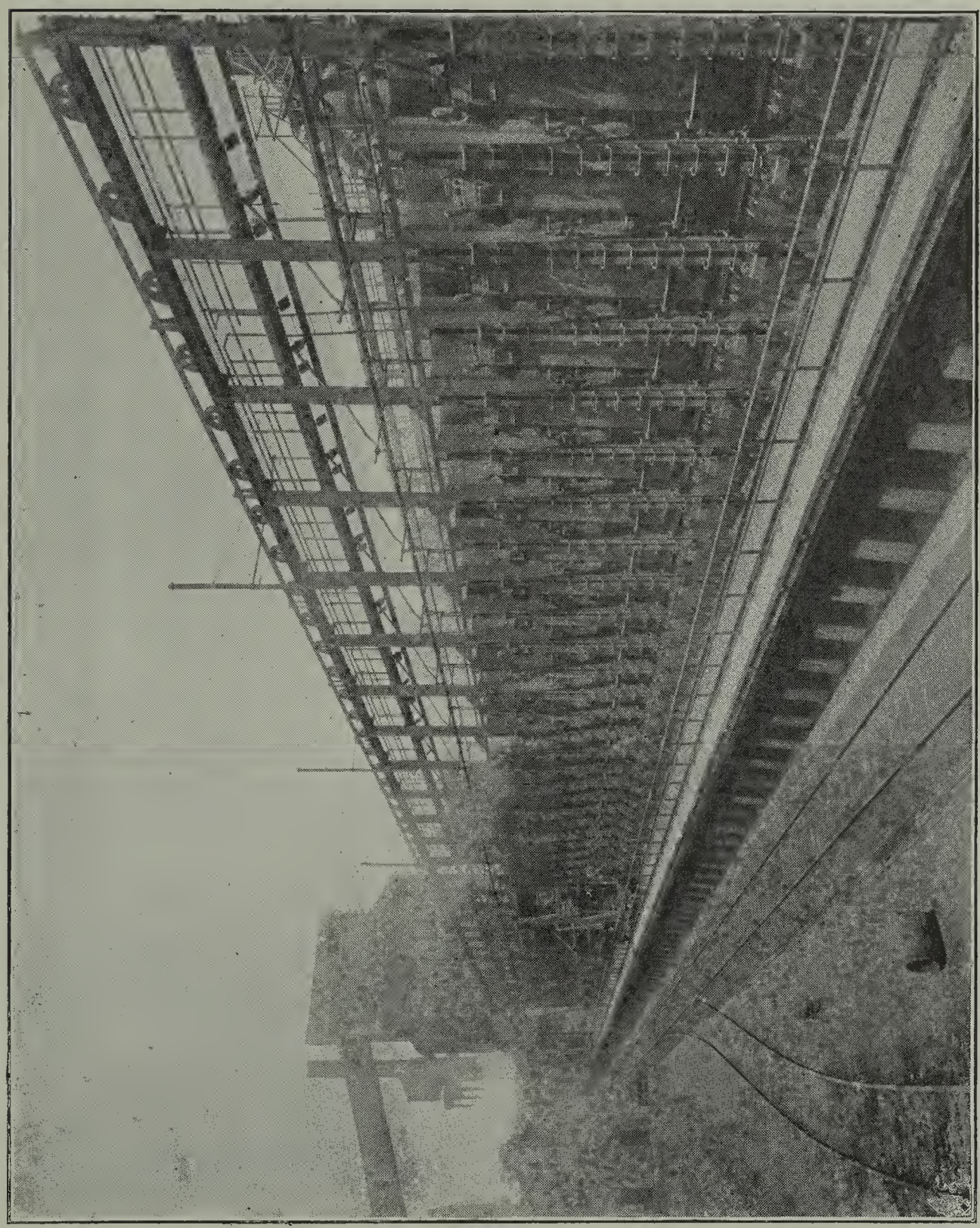

FIG. 3.—Discharge Side of Ovens and Coke Wharf at Left.

Each oven is designed for a charge of fifteen tons of pulverized coal, and to carbonize this coal in any period from sixteen to thirty hours as desired. The capacity of the oven and the uniform coal charges are points that are worth emphasizing. At the Ford plant

not only is the daily average charge per oven uniform but there is very little variation in the weights of coal charged in the different ovens. The regularity maintained in this operation is shown by Fig. 4, which gives average daily weight of coal charged per shift. This curve is posted in the foreman's office and closely watched by all three shifts.

The size of an oven is determined by the amount of coal that it can successfully carbonize. Size has so far been an index to the progress of the industry, increasing capacity resulting in lower unit costs. This because the plant, exclusive of ovens, and force required for operation and maintenance of complete plant are fixed and independent of oven capacity. That is to say, the power plant, byproduct

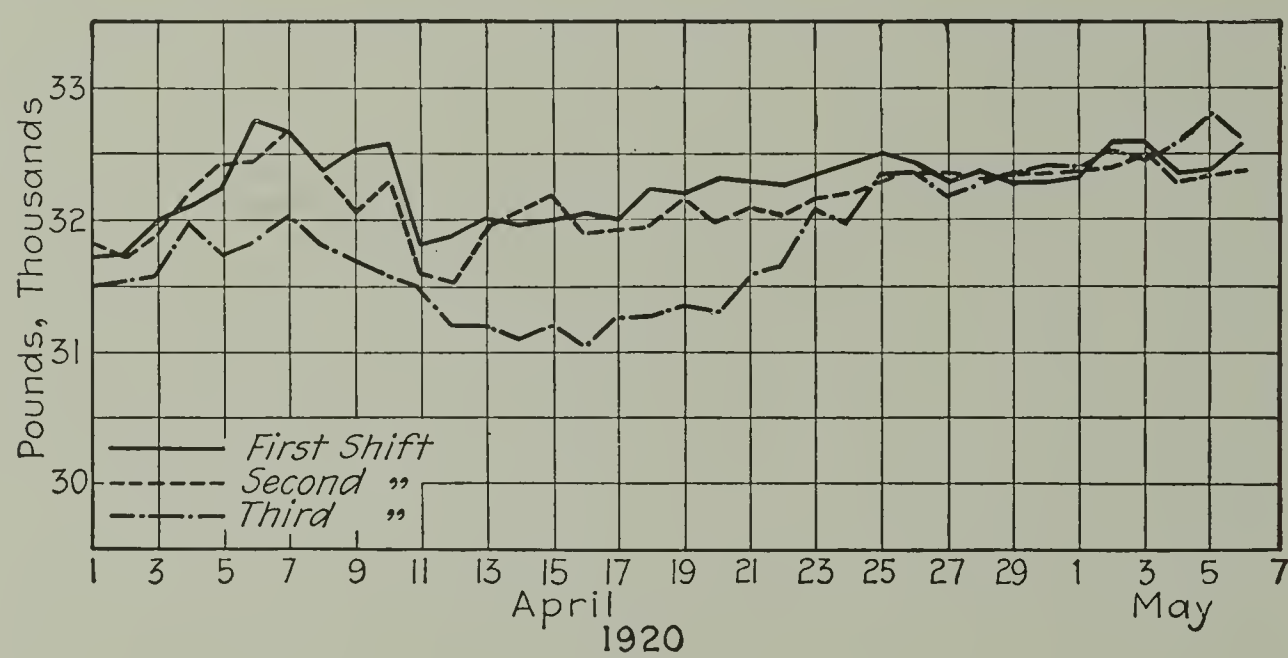

Fig. 4.

recovery apparatus, piping and other machinery will be practically the same for any given plant regardless of the capacity of its ovens, while the number of workers will be almost the same. The increased tonnage due to larger capacity of units will therefore give its yields at little or no cost of production.

Operating on an eighteen-hour schedule the Ford plant has a daily capacity of 2400 tons of coal. Were these ovens of 12-ton size the capacity of the plant on a like schedule would be 1920 tons. In a thirty-day month this would mean that the 15-ton unit plant would carbonize 14,400 more tons of coal than the smaller unit plant. The yields from this increased tonnage would be about 10,000 tons of coke, 345,000 pounds of ammonium sulphate, 45,000 gallons of light oil, 115,000 gallons of tar and 86,000,000 cubic feet of surplus gas. Figuring that the value of the coke recovered would cancel the cost

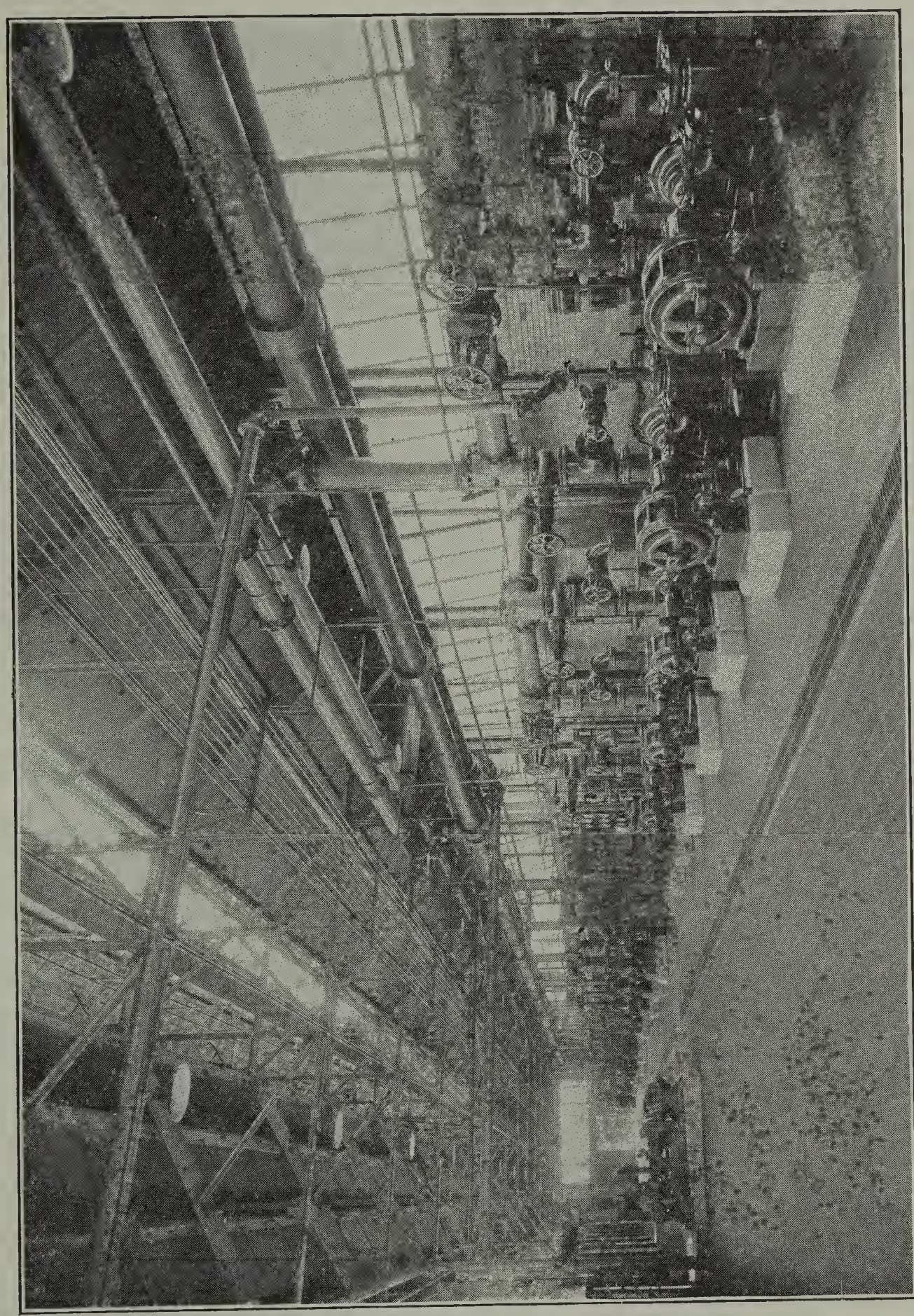

FIG. 5.—By-product Pump House.

of the additional coal and cost of producing byproducts there would be a net gain something like this:

345,000 pounds $(NH_4)_2SO_4$ at 5 cents per pound..	$ 7,250
40,000 gallons light oil at 15 cents per gallon.....	6,750
115,000 gallons of tar at 4 cents per gallon.....	4,600
86,000 M. cubic feet gas at 20 cents per M.....	17,200
Total monthly gain.....	$45,800

It is true that the initial cost of the larger plant would be greater, but the returns just enumerated would yield handsome interest on the additional capital required.

Ammonium Sulphate

The recovery of ammonia at the Ford plant is performed by the Semet-Solvay direct ammonium sulphate process. This process, which represents over eight years' extensive experience with direct methods, marks a notable achievement in chemical engineering. The process is direct in procedure, practically automatic in operation and produces a pure white salt. The high yields which are obtained are readily explained by the direct manner in which the gas is treated and by the control of the ammonia reactions.

In the first place, each oven is properly filled with coal, as previously described, so that favorable conditions exist at the start. The coke-oven gas upon leaving the ovens travels a short distance from the hydraulic main and then passes through a two-compartment cooler. From these coolers an exhauster (Curtiss steam turbine) takes the gas and sends it under pressure through a tar extractor of the P. & A. type, then through another two-compartment apparatus, called an economizer, from which apparatus it goes to the saturator. The gas leaves the saturator minus its ammonia, is freed of acid and then cooled for benzol recovery. This is the full journey of the gas so far as ammonia is concerned.

The gas enters the two-compartment cooler at a temperature slightly above 80° C. In the first compartment the temperature is lowered about 30° C. and in the second compartment it is brought down to 30° C. This temperature of 30° C. has been found to be the critical one for proper condensation in conjunction with minimum effort for subsequent heating. The cooling medium is a weak ammo-

nia liquor, which, traveling over grids counter-current to the gas, is very efficient. The strength of this liquor is maintained so that only a minimum amount of NH_3 will be absorbed in the cooling of the gas and the condensation of the light tars. Separation of the tar and liquor is effected in the coolers, which have a large base, by means of decantation. The tar is drawn off from the bottom and

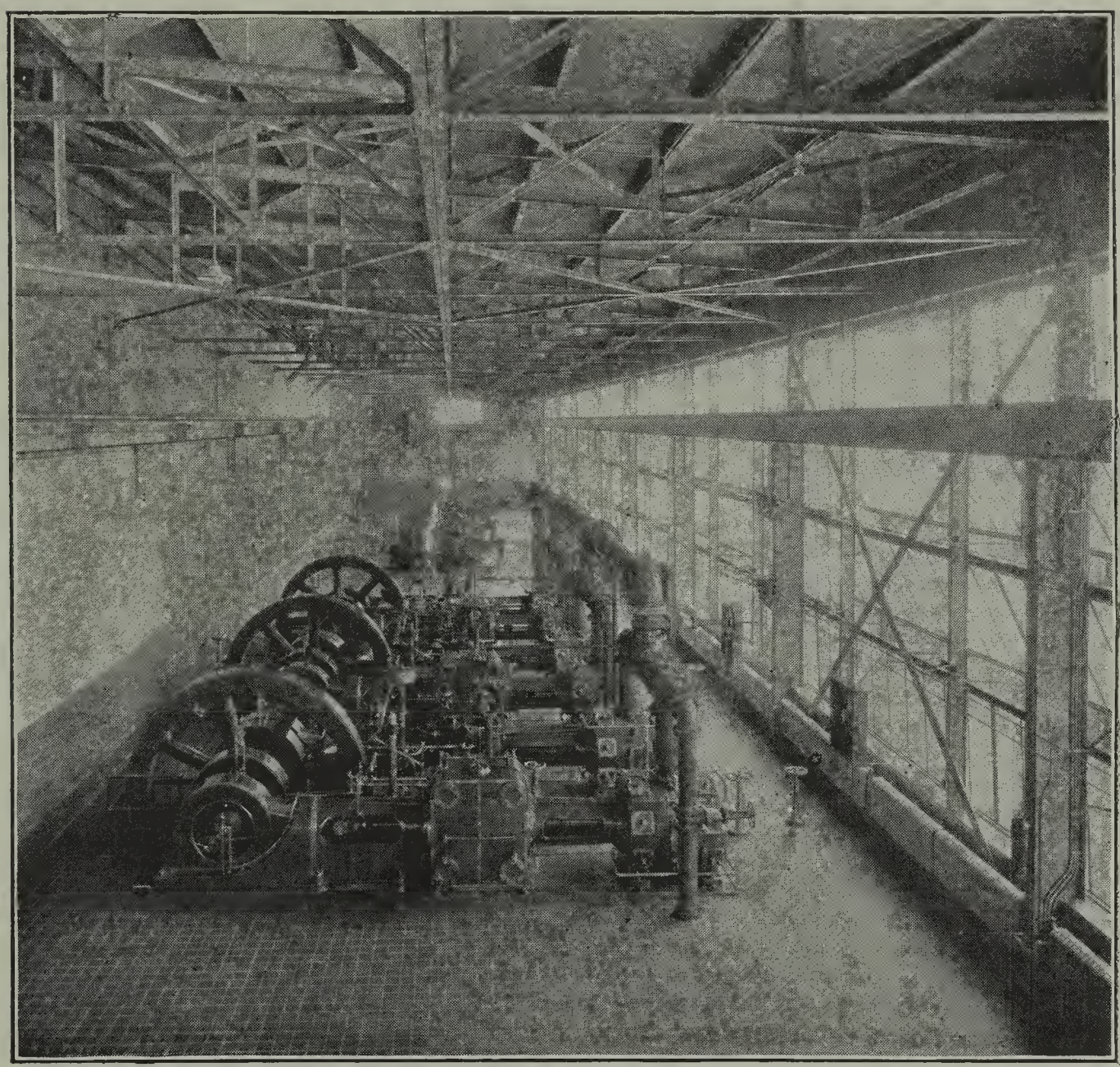

FIG. 6.—Exhauster and Compressor Room.

runs to a decanter, while the liquor entering the suction pipe of the pump at a higher point is sent through cooling coils and then back to the gas cooler. Each compartment of this cooler has its own circulation. A special constant level overflow device maintains a constant volume of liquor for circulation by carrying away an amount equivalent to that added by condensation and absorption of ammonia.

Ammonia thus held in solution has to be liberated by steam and lime in a still, from which it returns to the gas at inlet to saturator. With this exception the process is "direct."

The Curtiss steam turbine, whose primary function is that of an exhauster, serves in a threefold manner for in pumping the gas it is

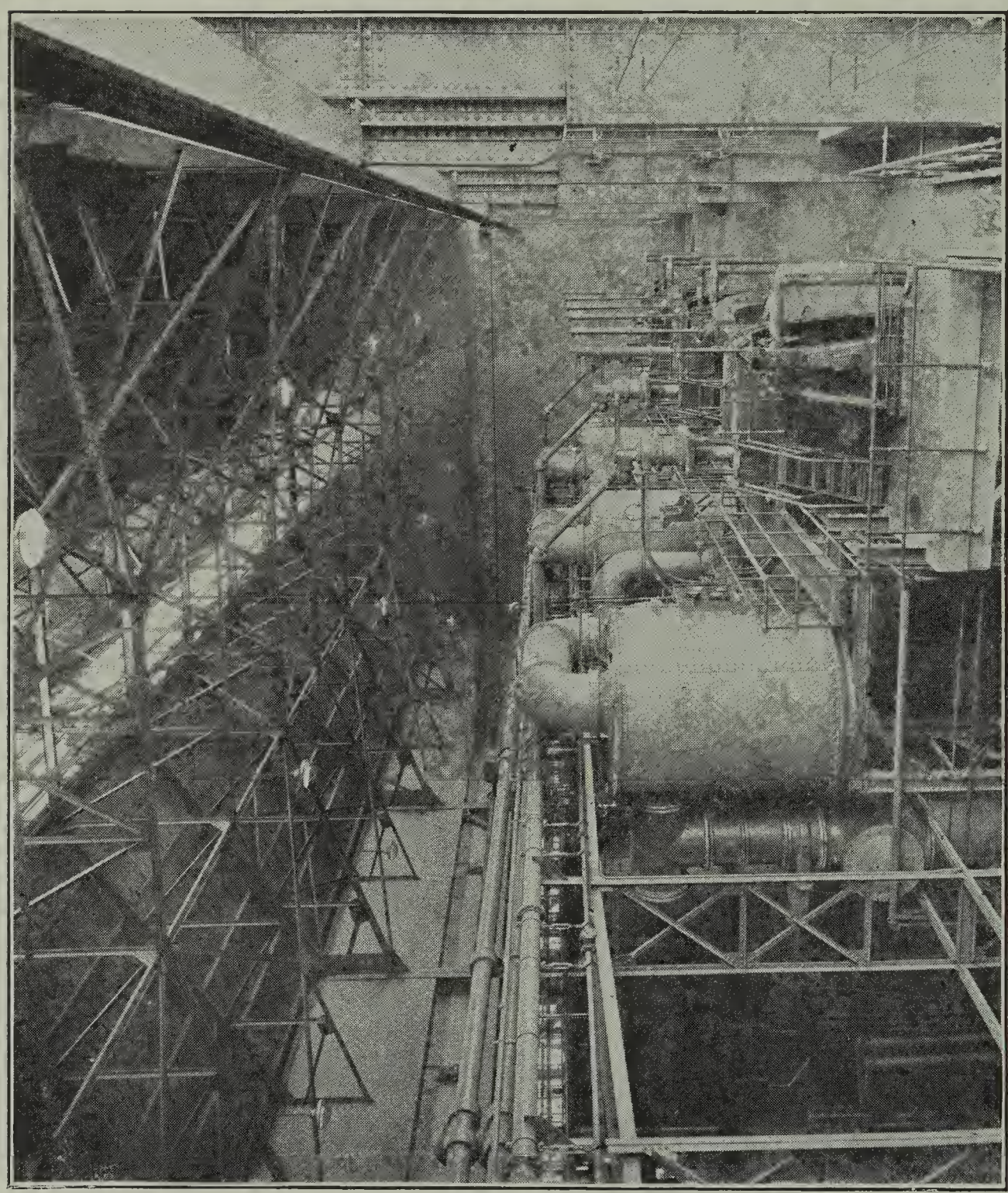

FIG. 7.—Direct Sulphate Apparatus.

at the same time an efficient tar extractor. Due to heat of compression, the gas leaves the turbine at 50° C., or about 20° C. higher than it entered. Thus the turbine is exhauster, tar extractor and heater combined. The P. & A. tar extractor removes the last trace of tar.

From the tar extractor the gas goes to the economizer, where it is brought in contact with the liquor of condensation from the hydraulic main to pick up and restore to the gas some of the water of condensation and free ammonia; the gas leaving the economizer is at the proper temperature for the sulphate reaction.

The clean gas at 70° C. enters the saturator, which contains sulphuric acid of 45 g.p.l. strength, that is nearly normal acid. The saturated acid is lifted by means of an air ejector into a sludge tank in which crystallization takes place and the unsaturated acid drains back to the saturator. The salt goes to a centrifugal, where

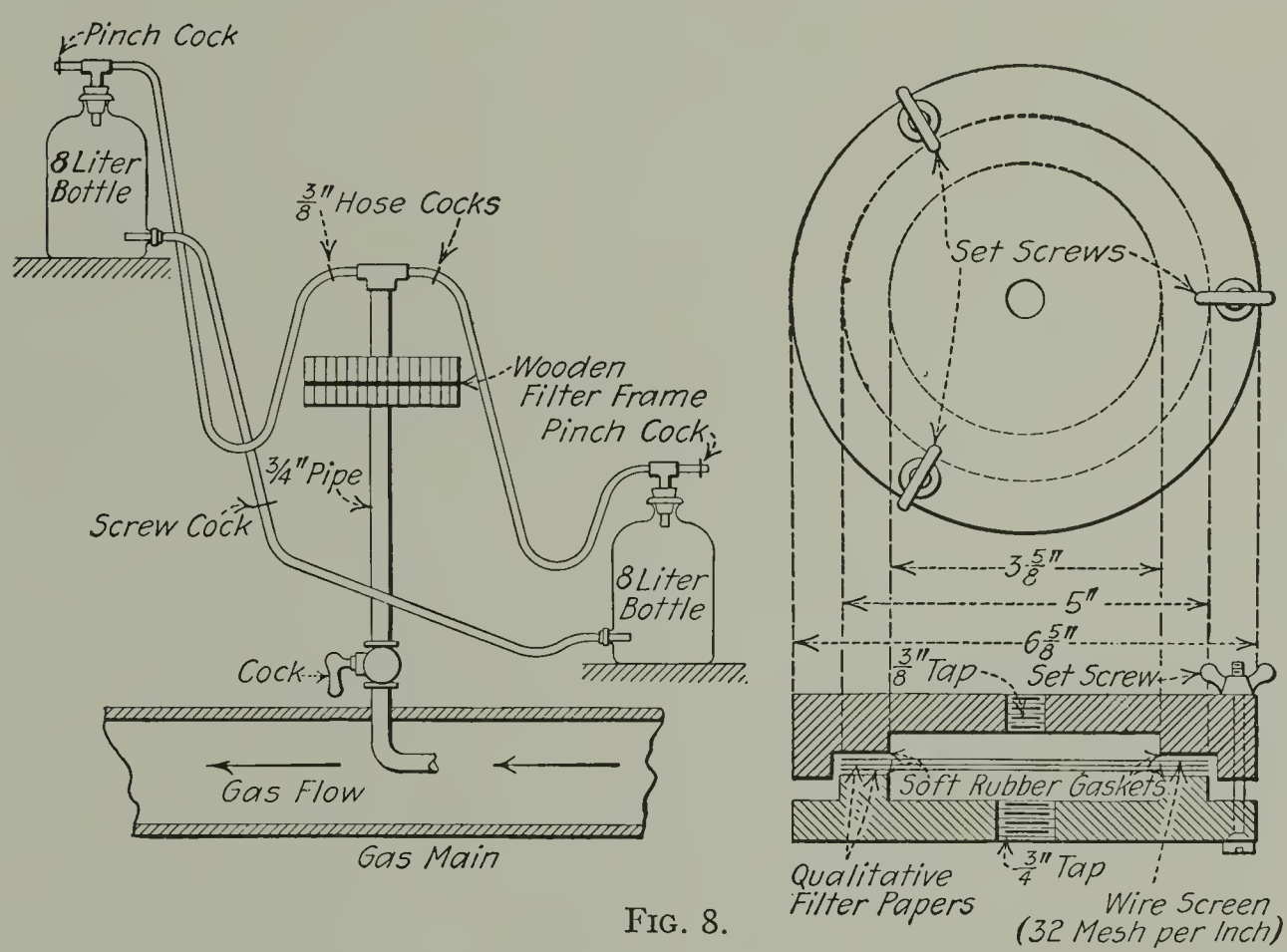

FIG. 8.

it is first dried and then washed with water. It is dumped from the centrifugal into barrows, weighed and conveyed to a large hopper, from which it is handled into storage by an overhead crane.

A small stream of fresh acid (60° Bé.) flowing into the saturator keeps the strength at the proper mark. With acid of the proper strength and gas at the proper temperature objectionable crystal formation does not take place in the saturator. The small amount of crystals that are bound to form on metal surfaces are not permitted to accumulate. Once each day for a few minutes the acid strength is built up to 125 g.p.l. and thus all crystals are dissolved and a clean saturator is maintained.

The results obtained at the Ford plant are indicative of the progress that this process makes in ammonia recovery. The high yields as shown in the table of operation data were obtained from a coal mixture containing 20% low volatile coal. From straight high volatile coal even higher yields may be expected.

As important as the yield of a byproduct is the cost of production. The unit cost is the test that tells the tale. During the month of April this plant produced over 1,500,000 pounds of $(NH_4)_2SO_4$ with an operating force of five men per eight-hour shift and one foreman. This foreman also has charge of the light oil plant.

One of the most essential points in a direct ammonia sulphate process is clean gas. Practically all the treatment through which the gas passes preparatory for entrance to saturators is made with the one purpose of obtaining clean gas. Upon the success of this treatment the purity and color of the sulphate depends. Hence the vital question is, "How clean is the gas?" To determine this the filter paper method devised by the Semet-Solvay Co. has been found very valuable. The apparatus, which is called the tar camera, needs little description other than that given in Fig. 8.

FORD OPERATING DATA 1920

ACTUAL RESULTS OF THE SEMET-SOLVAY DIRECT AMMONIUM SULPHATE PROCESS.

Date.	Dry Coal Charged, Tons per Day.	Coal Moisture Per Cent	Sulphate Yield, Com. lb. per Ton.	Per Cent NH_3 in Sulphate	Acid Consumed per lb. $(NH_4)_2SO_4$.	Per Cent Free Acid in Sulphate.	Per Cent Moisture in Sulphate.
January	1,813	5.2	25.7	25.01	1.07	0.169	2.25
February	1,813	4.4	26.5	24.94	1.01	0.135	2.42
March	2,030	4.0	25.9	25.00	0.95	0.125	2.46
April	2,022	3.5	25.8	24.99	1.00	0.112	2.16
May	1,911	3.5	26.8	25.00	1.02	0.151	1.84

An apparatus is here shown by means of which a known volume of gas can be drawn through filter paper and a comparison made of the color produced on the filter paper to indicate the degree of purification of the gas. As usually performed two filter papers are used for each test to absorb the tar from 8 liters of gas.

The amount of tar carried by the gas should be reported by comparing these filter papers with a photographic scale, similar to that used in any color comparison quantitative test. Or where great accuracy is required the determination is made by weighing the filter papers before and after the picture.

This apparatus can also be used for the determination of H_2S in gas. In this test the filter papers used are, of course, moistened with lead acetate.

Surplus Gas

The method employed for the preparation for sale of the surplus gas from the coke-oven plant is determined by the specifications which the gas has to meet. The general trend in the industry is toward the elimination of candle-power specifications and lowering the calorific value of the gas required for cities. Canada has now permanently adopted a standard of 450 B.T.U. and no candle-power. Only three of the larger cities of the United States still cling to a high-candle-power specification. This development is in direct line with the conservation of the natural resources of the country and is to the economic advantage of both producer and consumer of gas. It is no longer good economy to enrich gas with benzol to produce candle-power when the requirements for motor fuel are rapidly outstripping the supply. Money spent for enrichment of gas is practically all wasted as, with very few exceptions, the consumer derives no benefit therefrom. The purchase of special coals or the separation of the rich gas from the lean, or any other operation involving cost, to increase the calorific value of manufactured gas brings no benefit to the consumer, who must, of course, pay for this increased cost, and the Public Service Commissions and gas manufacturers should join in the determination and adoption of the standard of calorific value which permits a million B.T.U. to be delivered to the consumer at the lowest price. Of course, gases containing high percentages of nitrogen, like producer gas, are not to be considered in this discussion. This argument is illustrated by the following table, which shows the B.T.U. per cubic foot in the various gases when mixed with the theoretical amount of air required for their combustion. This mixture of gas and air is what the consumer actually burns, so it is clear that any of these gases, when properly burned with the correct percentage of air, will give the same results.

	Natural Gas.	Oil Gas.	Retort Gas.	Coke-Oven Gas.	Carburated Water Gas.	Blue Water Gas.
B.T.U.	91	93	91.7	91	92	88
Flame temp., deg.	1,852	1,915	1,896	1,892	1,914	1,928

So the real point of interest to the consumer is which gas can be furnished to him at the lowest cost per million B.T.U.

In several cities, however, the legal standards still require the delivery of gas of high candle-power and high B.T.U. content, and the gas from the Ford plant has to meet the standard of 18 candles and 600 B.T.U.

Light Oil and Gas Enrichment

The recovery of light oil at the Ford plant is so closely related to the enrichment of gas that these two subjects can well be treated together. As is usual in plants where surplus gas of high calorific and candle-power specifications is sold to public utilities, the rich and lean gases follow parallel but separate paths throughout the by-product recovery system. Up to the benzol scrubbers they are treated exactly alike, but from here on the treatment differs.

It is a comparatively simple matter to obtain large yields of surplus gas that will pass the average B.T.U. requirements, which have recently been lowered in most states. In such cases it is possible to remove practically all the light oils from the gas, and if so the rich and lean gases can be treated alike in the recovery of benzol, or the gases may be treated without separation, if the calorific standard permits. In being freed of its light oil the surplus gas is lowered in B.T.U. value, but at the same time it has all of its naphthalene removed. This treatment gives a gas suitable for distribution and, if separated, of 590 to 600 B.T.U. value. Such a gas meets the requirements of many cities which retain a high calorific standard, but it will not pass a high candle-power specification, and where such exists it is necessary to produce a very high-grade gas. Proper oven operation will yield such a gas, after which this quality must be maintained and delivered to the city without loss. For distribution it is essential that this gas be free of $C_{10}H_8$, but it cannot stand the loss of any

other illuminant. Of course, all the light oils could be washed out, freed of naphthalene and then used to enrich the gas to the proper mark. A high-grade gas would result, but the process would be rather inefficient and very expensive. The correct way is to take out the $C_{10}H_8$ without removing the light oils. This is accomplished at the Ford plant by the standard Semet-Solvay apparatus and methods. The procedure is as follows:

The lean gas, upon leaving the saturator, is cooled and enters the benzol scrubber at a temperature of about 25° C. In this tall tower it is completely stripped of its light oil content by being washed with an absorption oil of like temperature. This absorption oil, straw oil or ordinary gas oil, is circulated counter-current to the gas flow and leaves the scrubber containing about 2% of light oil.

The rich gas, upon leaving the saturator, is likewise cooled and enters a benzol scrubber at the desired temperature. Here it is washed by one-half of the benzolized absorption oil from the lean scrubber, the other half of this oil going directly to the light oil still. The small circulation of benzolized oil absorbs all the $C_{10}H_8$ from the gas, also some toluol and xylol, but removes very little benzol. Thus the gas is purified of $C_{10}H_8$ without serious loss of other illuminants. The drop in B.T.U. and candle-power, due to this treatment, are so slight that very little enrichment is necessary. According to the latest figures, only 0.027 gallon of light oil is vaporized per 1000 cubic feet of gas to bring the gas above specifications.

FORD OPERATING DATA, 1920

Surplus gas, light, oil and tar yields.

Date.	Dry Coal Charged, Tons per Day.	Total Gas per Ton of Coal, M. Cu.Ft.	Gas to City per Day, M. Cu. Ft.	Candle Power Initial Rich Gas.	Candle Power Gas to City, Official	Light Consumed for Enrich, Gal. per M. Cu.Ft.	B.T.U. Gas to City.	Light Oil Produced, Gal. per Ton.	True L.O. Yield, Gal. per Ton.	Tar Yield, Gal. per Ton.
January	1,813	10.53	9,959	12.83	18.08	0.33	636	2.32	2.65	6.02
February	1,813	10.39	10,135	13.82	18.17	0.14	647	2.35	3.74	8.09
March	2,030	10.63	10,004	14.05	18.14	0.10	646	2.61	3.76	8.84
April	2,022	10.50	9,906	14.27	18.21	0.10	638	2.43	3.68	8.64
May	1,911	10.04	10,518	15.12	18.21	0.05	643	2.42	3.45	8.51

The most important feature of this surplus gas operation is the uniformity of results. Not only has the surplus gas yield been high, as will be noted from table of operating data, but it has been a yield of high-grade gas. That is the important fact, for the yield of sur-

plus gas means nothing until compared with the quality. Furthermore, this yield has been almost constant in amount through the varying speeds of operation. Every day from January 1 to June 1 the gas company has received practically 10,000,000 cubic feet of gas from these ovens—gas that has always been above the standard. This gas has been produced and delivered with scarcely any variation in B.T.U. or candle-power values. The uniformity of these results appears remarkable in comparison to those obtained only a few years ago, but shows what can be expected from modern ovens with advanced knowledge and methods for regulation. The maximum gas recovery which is here shown is one reason also for the uniformly high sulphate yield.

A description of the light oil still is hardly necessary, as it is of the standard Semet-Solvay type. No fractionation is made, but the light oil is purified, washed and redistilled and sold as motor fuel. A satisfactory motor fuel consisting of benzol, toluol and xylol, mixed with an equal amount of gasoline, has the following distillation results:

Boiling Point, 71° C. Sp.gr. at 16° C., 0.811

Off At Deg. C.	Per Cent	Off At Deg. C.	Per Cent
85	10	114	60
88	20	130	70
91	30	154	80
96	40	195	90
103	50	218	95

Loss on distillation, 2 per cent. Residue, 3 per cent.

During the switchmen's strike there was a gasoline shortage in Detroit which caused some worry but little or no inconvenience, due to the fact that the Ford plant was able to release 300,000 gallons of purified light oil for motor fuel. Tank wagons from the various companies came to the plant for oil and then distributed it throughout the city. Thus a serious situation was averted.

The light oil that is recovered by the method described comes mainly from the lean gas. The true yield is therefore the sum of the oil produced and the oil left in the rich gas. This total would mean a high commercial yield, and one that would be possible wherever the gas specification was below 600 B.T.U. with no candle-power requirements.

Tar

The old-time problem, "What is to become of the tar?" has apparently been solved satisfactorily. With the enormously increased supplies the market has kept pace and to-day tar is selling at a decidedly higher price, but yet somewhat below its true value. Tar lends itself readily to a variety of uses, many of which are just beginning to be appreciated. The Ford experience affords an interesting illustration in this respect.

The original boiler equipment contained eight 400 H.P. Wickes boilers, arranged for gas firing. The demand for gas was so heavy that tar was utilized in its place most satisfactorily and at a decided saving over coal, the value of tar being taken at 5 cents per gallon. When using tar the pump at the storage tank is run continuously, so that there is a constant circulation sufficient to meet the highest peaks and yet allow excess tar to be bypassed from the discharge to the suction line. In order to keep the tar hot the discharge line is wrapped with two 2-inch steam lines and the tar reaches the boilers at a temperature of 90° C. At that point superheated steam is used to raise the temperature to 100° C. and by means of steam injectors delivered to the tar burners.

When the price of fuel oil became almost prohibitory the Ford company began experimenting with tar to take the place of oil in the heat treatment of forgings, etc. This worked out so satisfactorily that the company expects shortly to be using 15,000 gallons of tar per day, which will do the same amount of work as the 25,000 gallons of fuel oil formerly used. Part of this is due to the higher efficiency of the tar and the remainder to improvements in operation. This tar is as it comes from the byproduct coke plant, no further refinements being necessary.

In conclusion, I wish to acknowledge the assistance given by A. A. Kelkenney, superintendent of the Ford coke plant, in preparing the operation data and curves shown here and to express my appreciation of the courtesies and assistance given me by his organization.

The Solvay Co.,
Indianapolis, Ind.

AMERICAN PROGRESS IN DENDRO-CHEMISTRY

By H. O. CHUTE

Read at the Montreal Meeting, June 28, 1920

It would seem appropriate that on this visit of the Institute to Canada something be said as to the chemical products of wood as the forests of Canada are still one of her greatest assets and owing to the fact that their development on a large scale was later than that of the United States she has been enabled to profit by the mistakes of her southern neighbor and has done so in several ways leading to a conservation of forest resources and a better development of them, particularly with regard to the chemical products.

The World War showed America behind Europe and particularly Germany in many branches of chemistry but not in dendro-chemistry, and England early turned here for a supply of acetone for cordite, as America was the sole source of supply available and furnished nearly all used during the war and all during the early stages.

All chemical industries of the forest are by-product industries, or should be such, for nearly all woods are more valuable for timber and lumber than for their chemical products. The chemicals are therefore made from such pieces as, from their shape and volume, are not useful for lumber.

In those industries where the chemicals are obtained before cutting the tree, the chemicals, for example turpentine, should be obtained in such manner as to preserve the timber value of the forest. An example of this is the Herty cup system of turpentining which conserves the timber as compared with the older process of "boxing."[1] Forest chemical products are divided broadly into educts and products; the former existing ready formed in the wood and the latter being the product of chemical treatment. Many educts are really pathological formations.

Another broad distinction divides them into products which are separated from the wood as a sap, gum, resin or latex which exudes

[1] See U. S. Dept. of Agr. Forestry Bull., No. 90 and Chem. Ab., 1912, p. 1847.

from a wound and those which must be removed from the wood by cutting it and treating it chemically. Some products are removed both ways, for example turpentine and wood turpentine. The latter name refers to the product removed from the wood after cutting it.

Chemical products may be produced from the wood itself or from the bark, leaves, knots or roots.

Another broad distinction of products are those easily volatile or volatile with steam and those which are not. An example of the first is camphor, which is always extracted by distilling with steam.

The wood structure itself is of ligno-cellulose. The cellulose is a carbohydrate; what the lignin is is not certain as the chemists are still fighting on the question. In nearly all woods can be found some resins, terpenes and tannic acid but the quantity and proportion varies widely.

Cellulose

By far the greatest chemical product of wood in quantity and value is cellulose and it is the chief raw material of paper at present.

During the great war the Central empires were compelled to use wood cellulose for powder making and for twines and for clothing. We did not use any wood cellulose for powder on account of the large supply of cotton but experiments were proceeding along that line with promise of success.

In Germany it was even proposed to use wood cellulose for cattle food.[1] They found that if the lignin was taken from the wood substance by using the ordinary pulping methods, the cellulose was digestible if mixed with some other feed. It is probable that this was anticipated by the Yankee who painted excelsior green for horse feed.

Those of us who are old enough can remember the cotton famine in the north during the United States Civil War and that grocery twine made of paper was used commonly up till the eighties.

Woop Pulp for Paper

From the invention of papyrus till two generations ago paper was made from fibres of reeds and plants and wood cellulose was never utilized by man for paper though the wasps and hornets were making a pretty good quality of paper from wood long before his advent.

[1] Ch. Ab., 1919, pp. 1504 and 2067.

The manufacture of wood pulp originated in the United States and Americans invented most of the necessary processes.

There are four principal processes of making paper pulp from wood, namely the ground wood process, the soda method and its near relative the so-called sulphate process and lastly but of most importance is the sulphite process.

Ground Wood Pulp

This method of making pulp consists in holding on a grindstone a " bolt " or stick of wood at an angle and while keeping a strong stream of water on the stone the wood is ground down to fibres. It is preferable to steam the wood first and the U. S. Forest Products Laboratory recommends boiling the wood.[1] The Canadian Forest Product Laboratories have shown that ground wood absorbs 52% of the spruce produced.[2]

The invention of ground wood has been ascribed to Keller and Voelter who exhibited the machine and product at the Paris Exhibition of 1867 but the Canadians have claimed that it was invented there, by Chas. Finerty Sackville in N. S.,[3] though the previously cited publication attributes to Alexander Bunton the first installation at Valleyfield, Can. It is also said that the process was installed at Chesterfield, Mass., in '67. Modern magazine grinders have superseded the cruder machines but the grindstone still does the actual work of grinding the pulp. Much water for power is needed and also for cooling the stones.

White spruce is the preferred wood though nearly 50% balsam may be mixed with it and even a little birch has been used. But this grinding produces only a separated wood fibre and any color or impurity must remain in the product, therefore a soft white long fibred wood free from gum and resin is best.

There is no chemistry in the process itself but there is the bark by-product which we will show later is of importance for tannin extract. The U. S. Forest Products Laboratory investigations show that the bark contains from 8.34% tans up and they estimate that 55% of our tannins could be recovered from paper wood barks.[4]

[1] Ch. Ab. 1918 p. 1122 & U. S. Dep't. Ag. Bull. 343.
[2] Pulp and Paper Mag., Can., 1919, p. 3.
[3] Ch. Ab., 1915, p. 1930.
[4] C. A., 1919, p. 2144.

Ground wood forms from 70% to 90% of our newsprint and such building fibre sheets as " Beaverboard " are largely composed of it. For higher grade papers it is not favored. It is seldom bleached.

Soda Pulp

This is made by chipping wood and boiling it under pressure in a steel digester with caustic soda. It makes a fine soft pulp easily bleached suitable for use in filling book and bond papers. It is also largely used in good blotters. One of our members[1] has given a good description of the process as it was then worked in Canada. It was shown that the Windsor Mills, P. Q., began the manufacture shortly after the mills at Manayunk, Pa., and Royersford, Pa., where the first American manufacture of soda pulp began. In 1854 Chas. Watt and Hugh Burgess received a United States patent for pulping shavings by treatment with caustic soda and this is the birth of this industry. The United States Supreme Court held the patents invalid but this was owing to their having a poor patent attorney. The Jordan engine was also invented there.

It is probable that the introduction of the multiple effect evaporator invented by Homer T. Yaryan of Toledo[2] into the art contributed much to its profitable outcome. The N. Y. and Pa. Paper Co. of which Col. A. G. Paine was president did the necessary work to successfully demonstrate the savings of the operation of the apparatus.

While a vacuum pan was introduced in America at Plaquamine plantation in 1831 and the multiple effect apparatus is the invention of Norbert Rilleux, a creole Frenchman born in Louisiana who introduced it in 1843 at Bayou La Fourche and at Myrtle Grove plantations and had fifteen installations in Louisiana in 1851; yet, until the Yaryan apparatus was introduced into the soda pulp business all the evaporation was done rather crudely. The writer dismantled a soda pulp factory at Fenelon Falls, Ont., in 1898, to substitute a wood distillation plant. It had no improved evaporation system but had it had such a system it would have been profitable. Here was a failure due to neglect to progress and put in improved apparatus.

The latest improvements in this industry have been described

[1] J. A. DeCew, J. S. C. I., 1907, p. 561.
[2] See trans. A. I. Ch. E., Vol. X, p. 206.

lately in Canada.[1] Aspen is the favorite wood though the coniferous woods such as jack pine are used. They are harder to decompose and do not bleach as well. The hard woods such as beech and maple and birch are worked successfully. On account of their weight they give a large tonnage per cord.

The chemical engineering problems connected with the process are largely due to the problem of recovering the soda used and putting it into condition for re-use.

An idea of the amount of evaporation necessary may be had by noting that more than one-half the weight of the wood is dissolved as organic combinations with soda. The spent liquor of 10° Bé. as sampled contained 14.4% solids. When concentrated in the Yaryan evaporator to 40° Bé. it contained 37% water, 34% organic matter, 26.7% soda and 2.3% other mineral matter.

The soda was three-fourths combined while the other fourth was carbonate.

For every ton of pulp made 12 tons of water must be evaporated.

The first evaporation is in multiple effect but after it gets to 40° Bé. it is too stiff to work further and it is fed into a rotary furnace like a cement kiln, they were made about 15 feet long but now they are 30 feet long and 9 feet diameter. These will produce 50 tons of black ash. A fire is kept up in front and seemingly the flame is always a reducing flame but much heat is generated from the combustion of the ash and is utilized in waste heat boilers.

Just why the soda cannot be smelted as is done in the sulphate process the writer does not know. The black ash is leached usually by diffusion processes and re-causticized. The counter current decantation system described in Vol. 6, p. 86 [2] has been applied in the causticizing and modern filters have been used to de-water the lime sludge. The writer saw this sludge dried in rotary drums to produce a substitute for English whiting but it is not white like English chalk.

Reclaiming the lime in rotary kilns, such as those just described,[3] has been used in one or two places but there is a fear of it. The author saw this operation very successfully carried on at Salinas, Cal., with calcium carbonate residues from beet sugar manufacture, and believes it will avoid a nuisance as well as be profitable in the pulp industry. There are losses all along the line and a recovery of 85% is good work.

[1] E. Sutermeister, Can. Pulp and Paper Mag., 1919, pp. 215 et seq.
[2] Trans. Am. Inst. Chem. Eng.
[3] Paper of Richard K. Meade.

By the counter current system of decantation the filter press receives the nearly extracted ash. This gives a concentrated solution of carbonate and a thorough extraction. Both multiple effect evaporation and diffusion are highly developed in the sugar art.

The residual carbon has for many years been utilized at one works on a small scale for making a commercial carbon and at least one manufacturer has developed a decolorizing carbon from it which has special value for some limited fields.

Quite a little experimental work had been done several years ago and a number of patents taken out on the production of acetate of soda from the black concentrated liquor and attempts were made to produce methyl alcohol and acetone from it. During the war two very extensive plants were put in to make acetone by destructively distilling it in presence of excess of lime. Reports are quite favorable but commercial work was not begun when the armistice was signed and both plants are now reported idle.

After mixing the 40° liquor with a large excess of lime the resulting solid mass was fed into a revolving cylinder 160 feet long and 6 feet diameter at the exit end. The entrance end was much enlarged so that it was about 18 feet diameter. It was of $\frac{3}{4}$-inch steel closed at each end and set in a fireplace. Another acetone furnace was 8 feet diameter and of the same general construction. Arrangements were made for the feeding in at one end of the mixed waste and lime and at the other end were arrangements for discharging the waste black ash and lime and also taking off the acetone vapors developed. Numerous fireplaces under the revolving retort allowed heat treatment and regulation. It was said that this process made more acetone from a cord of wood than could be obtained by wood distillation.

Some years ago the writer with others developed a process for increasing the amount of acetate in these wastes by carefully oxidizing the heavy liquor.

United States patent No. 1002034 describes the process which would of course increase the amount of acetone made in any subsequent process of destructive distillation.

Alcohol, acetone, terpines and other volatile substances are reported to occur in the vapors discharging during the cook. It has been feared that their recovery would be too expensive owing to the immense amount of steam which would have to be discharged. This is probably overestimated as by some little regulation all the volatiles could be removed with the loss of little steam. The con-

densation of the steam under pressure would heat up a large quantity of water which is useful. The further recovery by fractional distillation would be easy if the methods used in other industries are adopted. Later descriptions will be given of processes for working resinous woods to recover the resins and also to make pulp.

When the evaporation and burning to ash is so economically done that the heat is all furnished by the combustion of the organic matter or when acetone, and decolorizing carbon are by-products together with reclaimed lime and the volatile products such as alcohol and terpines are saved the chemical engineer will have made this an almost ideal process.

Perhaps the dust collecting systems described in "The Transactions," Vol. 8,[1] pp. 35 and 65 would give a further economy in chemicals. We shall see this working on soda recovery at La Tuque.

The Sulphate Process of Pulp Manufacture

In 1871 John Eaton of Brooklyn, N. Y., received a patent claiming the use of sodium sulphide in treating wood for pulp and got it by reducing the sulphate.

John Priestly of Philadelphia claimed at this time that he had worked with the sulphide and proved its superiority to caustic. The Eatons put up a plant in Brooklyn to work the process. The sulphate process was not a success till much later and the particular success of the process is in making "Kraft" pulp. This is said to be due to the stupidity of a Swedish workman who dumped a digester too soon as was then thought. The Superintendent of the factory though, ran it through a kollergang to reduce it and was much surprised to find it a strong and good pulp.[2]

The sulphate process, so called, is a modification of the soda process in which the losses of soda are made up by adding sulphate of soda to the causticizing tubs. On the next pass it is reduced to sulphide in the furnace so that the liquor is a mixture of sulphide, caustic and other thio compounds.

As we will see this process at La Tuque and we have had the operations of the plant described in Vol. 10, p. 177 of our transactions it is unnecessary for the writer to describe it further and prudence would dictate caution when there is the probability that any inaccurate statements may be so soon discovered.

[1] Trans. Am. Inst. Chem. Eng.
[2] Ch. Ab., 1908, p. 317.

However, should any inaccuracies of the writer appear it is only necessary to call attention to the extraordinary character of the La Tuque plant and its extraordinary technical management, compared to the standard practice,[1] Spruce wood is undeniably the best wood for the sulphate process but as various classes of pine are so well worked by this process it is very largely used. We were told that La Tuque uses the pine of the region. In several Pennsylvania plants the ordinary field pine of northern Virginia is hauled the long distance and worked seemingly better than any other available wood.

Several plants in the Southern states are making a success of the process operating on the long leaf pine offal from the saw mills.[1] When producing kraft there is the advantage that it makes a marketable paper direct so that any mill should find a local market in the wrapping paper field.

The problem of recovering the soda is the same in both processes and only differs usually in that the black ash of the sulphate process for the revolving furnace is dropped into a smelting furnace with air blast, the gases passing through the revolving furnace and supplying it with heat. No fuel is necessary to produce a fused cake of carbonate and sulphide of soda from the concentrated liquor except that supplied by the combustion of its own organic matter. A large surplus is utilized in disc evaporators and waste heat boilers. In fact one of the firms building this machinery claims to do all the evaporating and recovery by the heat developed by this oxidation or burning of the organic matter in the spent liquor.

Why the soda process ash is not fused in a smelter thus the author knows not.

Owing to the formation of mercaptans in large quantities this process is well adapted for such places as La Tuque and on the Southern pine barrens.

Both these processes are most economically carried on in connection with a saw mill using up those parts of the timber supply not suitable for lumber and utilizing the sawmill refuse for fuel. Owing to all solutions beng alkaline iron and steel vessels can be used without undue wear taking place.

It would even be possible to manufacture the chlorine and soda electrolytically if enough sawdust and other fuel were available. Later we propose to show that the soda pulp business led to the

[1] "Paper," Vol. 20, 1917, Carl Moe.

invention in America of the electrochemical manufacture of chlorine and soda.

The Manufacture of Paper Pulp from Wood by the Sulphite Process

The most important process of making paper pulp in America is the sulphite process. In 1866 B. C. Tilghman received United States patents claiming pulping the wood by the use of bi-sulphites. While he made paper, his process was not perfect and the mechanical means of working were not yet invented. In Vol. 1, p. 130 of our transactions are given specifications for sulphite pulp.

While Europeans worked on the process and got important results, it is probable that the American invention of using a cement lining for the digester made commercial success possible.

On our visit to Berlin, N. H., a few years ago we were shown all the essential details of the process and saw most of the apparatus at work.

At another plant recently, the practice was about as follows: Canadian barked spruce wood was chipped as usual and 18 cords put into a digester with 22,000 gallons of liquor containing 1.3% of bi-sulphites of lime and magnesia in the proportions of the alkaline earths found in dolomite stone. About 3% of free SO_2 was absorbed in this solution. After the usual cook during which the steam and SO_2 evolved passed to lead pipes and were cooled and the SO_2 re-absorbed; the residual liquor from the pulp contained about 12% of total solids. The writer does not know just what these are but knows some things they are not which they are said to be.

Firstly, in a proper cook there is no appreciable amount of either free or combined SO_2 in the liquor. There are substances which will reduce a small quantity of iodine and on acidifying they will distill over and reduce iodine but the oxidized product will not precipitate with $BaCl_2$.

Secondly, the free acid is about equal to 1/10 normal of which two-thirds is acetic acid. In a liquor with 10% total solids were found 0.857% ash of which 0.286% was CaO and 0.218% was MgO. The total SO_3 as determined by $BaCl_2$ was 0.010% but the total sulphur found on oxidizing and precipitating with $BaCl_2$ was 0.6825%. The tans were 4.13%. The reducing sugars were 2.5%. These were not all fermentable; the writer has observed an almost constant

ratio of two-thirds as being the proportion of fermentable to reducing sugars.

Utilization of Sulphite Waste

The waste liquor has been the subject of much work and the Institute has learned of the manufacture of alcohol from it as recorded in our transactions in Vol. 11, p. 55.

It has been used in America for core compounds, road binder,[1] making yeast,[2] alcohol and tans.

It would seem that if the proposed process of fermenting and concentrating to small volume were put in operation that perhaps yeast containing the nitrogen, alcohol, and tanning material could all be recovered and a purer tanning material thus produced. Producing all the above would be little more expensive than producing one.

Other By-products of the Sulphite Process.—All the spruce wood is barked and it is known that the bark contains some tannic acid. At least one company is putting on the United States market spruce bark tan extract under the name of "larch" extract. There are various tanning materials made from the sulphite waste sold under the names of "spruce" "muskegon," etc.

To produce a tan the lime must be removed from the waste liquor and this is done by sulphuric acid or sulphates as by using alum, etc. It is a singular fact that on concentrating a neutralized liquor calcium sulphate crystallizes out, removing the lime thus almost completely when strongly concentrated. The sulphates were not in the original liquor.

As a road binder sulphite waste is excellent on some soils containing certain clays. Without these clays it is perfectly useless as a binder. There is some protective colloid action here which is unknown but it would be exceedingly useful if it were well enough known to enable one to use the liquor with assurance of success for road binding.

Cymene.—It has been known for a long time that cymene was the terpine given off from spruce under the sulphite treatment but lately attempts have been made to utilize this for making toluol.[3] Thymol,[3] and carvacrol[3] are said to have been made from it. During

[1] C. Ellis, Pat. No. 15042538. [2] U. S. Pat. No. 1044615.
[3] J. Eng. and Ind. Chem., 1918, p. 259.

the war the sulphite manufacturers were asked to save the cymene but none or little was saved. It would appear easy to allow the condensate of water and cymene from the blow off to settle in a quiet tank while the SO_2 passed on for recovery. When the cymene came to the top the water charged with SO_2 could be removed from the bottom. This only requires a trap in the lead condenser line and a settling closed tank.

The manufacture of thymol from cymene has been patented [1] and somewhat developed in France. At present its price is very high ($14.20 per pound) and it is almost unattainable. It is considered a specific for the sleeping sickness.

As sleeping sickness produces an inability or lack of desire for work it would appear that the whole world now needs a thymol treatment.

Electro-chemical Development

Previous mention has been made of the fact that the paper pulp industry of the United States furnished the market for the product, the stimulus, and perhaps most of the money needed for perfecting the electrolytic decomposition of salt which has freed America from the European monopoly of chlorine and the near monopoly of caustic soda manufacture. In proof of this is the following quotation from an article in the Journal of the American Chemical Society of November, 1898, by Prof. Chas. Parsons, " E. A. LeSueur enjoys the distinction of having invented the first electrolytic process for the decomposition of NaCl which was commercial.[1] Since February, 1893, there has been a manufacture of chlorine and bleach at the Rumford Falls paper plant.

He began experiments in 1887, and in 1890 in the paper mills at Bellows Falls chlorine and bleach were made commercially.

We thus see that two paper mills were associated with this electrolytic process in its infancy and we have a number of members who were also pupils of this inventor who can perhaps enlighten us on its early history.

To the invention of graphitizing carbon by one of our members is due the great modern success of this industry as every type of cell relies on graphitized carbon for the anodes.[2]

[1] J. Eng. and Ind. Chem., 1918, p. 259.
[2] E. G. Acheson, U. S. Pat., 836355.

Other Products of Cellulose

Cellulose esters as nitrates are the basis of all propellant powders used for military operations. As before said the Allies did not utilize wood pulp but the Central powers were forced to use them almost exclusively and a sporting powder made from wood pulp was on the market for years before the war.

It is believed that wood pulps have been successfully used in making the pyro-cellulose plastics used industrially. The artificial silk industry using the xanthate or compound of cellulose formed by solution in caustic and carbon bi-sulphide is expanding rapidly in the United States. One of our members has developed this material for making tubes and films and it has been used for sausage casings which were exported to Europe and encased the genuine Frankfurter though the Coney Island hot dog seldom wore these clothes.[1]

Oxalates are made by decomposing wood by heat in the presence of a large excess of alkali. The U. S. Forest Products Laboratory[2] has shown that a yield of 74% oxalate could be made by heating with three parts of alkali to one part of wood and to 200° C. using southern pine. With oak the yield was 60%. Maple and elm yielded 14% acetic acid at the same time. By crystallizing out the excess sodium carbonate as decahydrate the oxalate was purified. A factory has operated in the United States for ten years but oxalate is now quoted at 60 cents a pound.

As a by-product of a sawmill; oxalate of lime would be the best form in which to manufacture and ship this valuable substance.

Sugar and Gums as Wood Products

North America is unique in having the only deciduous tree that produces sugar in commercial quantities. The acer saccharum, sugar maple or hard maple is well known as a producer of sweets and the Indians knew of its sweet sap and evaporated it down in earthen vessels to a dark sweet solid sugar. There is some question as to whether the Puritan Yankees or the French Canadian first learned the art from the Indians. A description of the Canadian industry

[1] Ch. Ab., Vol. 9, p. 3358; Cohoe, U. S. Pat., No. 1158400.
[2] Ch. Ab., 1919, p. 1923, and J. Ind. and Eng. Chem., 1919, p. 651.

has been recently published.[1] The industry is seasonal and as the production is so scattered no large factories can be installed at a profit yet some modern methods are used; even pipe lines convey the juice to the evaporator plant by gravity in favorable locations.

The yearly production is about 40,000 tons.

Palm sugar and toddy, the alcoholic drink made from it, are important in tropical Asia and contiguous coasts; 100,000 tons of palm sugar were refined at Asiatic ports last year and 10,000 tons were refined in Europe.

Sugar and Alcohol made from Wood Cellulose or Substance

We were shown in Vol. 8, p. 262, of the transactions by Pres. Little that, though the Braconnot process of hydrolyzing wood to sugars by acid was over one hundred years old and the eminent chemist Classen had induced large scale attempts here to work his process, yet only when American inventors modified the process was it a commercial success. The yields of the process are not positively stated by anyone but the writer was told by a practical workman that at a southern plant the yield of alcohol was about 11.25 gallons of alcohol per cord. One of our Canadian members has modified the process by using HCl.[2]

Gums.—Of the true gums—that is substances soluble in water and insoluble in alcohol, for example gum arabic the North American continent has no trees that produce any commercial article.

Gums, Resins and Balsams

These terms are used loosely in many cases to denote products which are not strictly what they are called. For example Canada balsam is really an oleo resin. It contains a terpine and a resin in solution; the same applies to " gum " turpentine which is a terpine saturated with a resin.

Canada balsam is known to all who use the microscope and for lens makers and others who cement glass; it is quite important as its index of refraction is the same as glass. Its other uses are quite restricted.

Oregon balsam is a nearly related product of limited use. While

[1] J. B. Spencer, Canadian Forestry Journal.

[2] C. A., vol. 6, pp. 1553 and 3329.

Canada balsam is quoted at $16 per pound the Oregon is quoted at $1.80.

Camphor.—While synthetic camphor is being manufactured to a considerable extent in the United States yet the price of camphor is now $2.4c and a monopoly of natural camphor is enjoyed by the Japanese. There are, however, a number of groves of camphor trees in Florida covering thousands of acres and perhaps in time they may produce a considerable product. The tree flourishes there.

Eucalyptol.—In southern California the Eucalyptus Globulus or Australian blue gum flourishes as can be seen by any outside movie scene. In Australia this is said to produce cineol or Eucalyptol but the writer tested pure oil from the "globulus" grown in California and it does not stand the U. S. P. test of solubility in alcohol prescribed. This indicates excess of the terpene phellandrene.

Eucalyptol is now quoted at 80 cents per pound for American and 90 cents for Australian.

Oil of Sweet Birch.—This is an oil which is largely methyl salicylate but it has a very pleasant odor and is quoted at $5.75 per pound. It is obtained by steam distillation of the birch bark. Both this and the true oil of wintergreen are subject to great adulteration particularly with the synthetic product, but while wintergreen oil is much higher even than birch oil yet experts can apparently tell them apart.

Styrax or Storax.—Our supplies of liquid storax were obtained from the Levan with no interest shown on our part to obtain it from our own forests till the war shut off the supply. The sweet gum "Liquidambar Styraciflua" found so plentifully in the south produces a similar product as can be seen by Thorpe as samples were exhibited in the Paris exhibition of 1878. The yield is two pounds per tree and it contains 35% cinnamic acid.[1]

The foreign is quoted at $4.00 per pound and the American brings only $1.85.

Turpentine

The Southern long leaf pine, the Pinus palustris or australis, which grows from Virginia to Texas along the seaboard produces the chief amount of "naval stores" used in the world. Turpentine, rosin and tar are called naval stores on account of their great use in wooden sailing vessels. The tar was used for calking and preserving

[1] J. Ind. and Eng. Chem., 1917, p. 770.

ropes. The turpentine was used for paints and the rosin had many like uses. For the calendar year there were exported $10,000,000 worth of turpentine and $20,000,000 worth of rosin.

This is not, however, the time and place to discuss the gum turpentine industry as the last preceding meeting of the Institute was held in the heart of the turpentine belt. It was observed there that the pine of the South is rapidly disappearing under the woodsman's ax. The present quoted price of turpentine is $2 per gallon while the pre-war average was 60 cents. Rosin was formerly the cheapest organic acid and was largely used as the soda compound in soaps. Its present price puts it at about where the fatty acids were in pre-war days. Present quotations are about 10 cents per pound.

During the United States Civil war the scarcity of naval stores led to the development in Canada of attempts to obtain "wood" turpentine from the pine called red pine in Canada and "Norway" pine in the United States. It is not the true "Norway" pine of northern Europe from which the "Russian" turpentine and "Stockholm" tar are made by destructive distillation but the stumps are quite rich in resinous matter. Some few attempts are made occasionally in Canada and the United States to utilize this "Norway" pine for producing wood turpentine but no great success has attended any of the enterprises as yet.[1]

We shall see at La Tuque the recovery of "steam distilled" turpentine recovered from the digesters while boiling the pine chips for pulp.[2] In Vol. 1, p. 216[3] we were given a rather full description of the wood turpentine industry as it existed then in the South and the writer in a tour of examination of the industry last fall saw few improvements over what was then described as the existing art. The author made a rather extensive tour of the Eastern Southern States in 1904 and examined into the status of the industry as it then existed. This embraced 55 plants running and abandoned.

At Wilmington, N. C., is the Spirittine Co. which traces its history back to the late seventies. It still exists and has gone into bankruptcy only a few times and at times has paid dividends from actual earnings. This can be said of only a few plants which can be counted on the fingers and perhaps using only one hand. This is a crude destructive distillation process putting "light wood" into round retorts and firing them till charcoal is produced and then

[1] Ch. Ab., 1911, p. 992.

[2] Ch. Ab., 1909, p. 1083.

[3] Trans. Am. Inst. Chem. Eng.

cooling and emptying them. The oils are crudely separated by a few old turpentine stills and the product has a limited market but the plant has paid from time to time. Many fantastic schemes for varying the process have been patented and tried and described.[1] No one has yet put in the well tried successful processes and apparatus of the hard wood industry. Till they do, the industry will never be on a sound basis. In the writer's opinion destructive distillation as practiced on the hard wood using the same machinery and the knowledge gained in this art will make a success of " wood turpentine" manufacture.

The " steam distillation " process recovers only a small quantity of the volatile oils. This is because only those cells cut open and exposed have their oils removed with steam. The solvent extraction plants have suffered the fate of all Soxhlet extraction plants which work industrially. Namely they either burn up or blow up. They also fail to recover all the solvent and leave some mixed with the turps. Any expert can, by shaking and observing the bubbles in a bottle of oil, instantly detect petroleum mixtures in turpentine.

An attractive process was patented by one of our members.[2] In this process the chipped wood is put in a digester and mildly digested with a dilute soda solution till most of the rosin is dissolved. The turps in the meantime distill off the digester and are condensed and saved.

When the rosin has dissolved, the solution of sodium resinate is discharged from the digesters and a stronger soda solution is put in and the usual soda process carried out. Thus, the resin does not materially interfere with the paper making.

The sodium resinate is treated with enough caustic to make a 6% solution which " salts out " the resinate of soda. This product is used for soap or the resin otherwise recovered. The strong caustic is of course used for a subsequent charge of wood. Here is a complete utilization of the cellulose, terpines and resins of the wood. Incidentally it has been found that the southern pine stump fiber when freed of the resins is particularly long and may be used for tarred paper. Any burned wood would not affect its value greatly as the color is of no importance owing to the final product being black. We will probably see at La Tuque the recovery of turps from the

[1] See Harper, Utilization of Wood Waste by Distillation, and Ch. Ab., 1909, p. 374.

[2] U. S. Pat. No. 1142992 to M. C. Whitaker, Jour. Ind. and Eng. Chem., 1914, April, pp. 289–298.

digesters. The production of turps by relieving the digester of gases was experimented on some time ago.[1] It is claimed that two-thirds of 1% of the wood may be recovered as alcohol.[2]

We have had pointed out to us[3] the possibilities of the coniferous woods being used in the manufacturing of chemical products.

During the war the Germans evidently made wood turps as one of them reports[4] that they seized the Polish and other plants and used prisoners for operating the kilns and gathering the wood.

Tannins and Dyewood Extracts

The discovery of the use of wood extracts for tanning and dyeing is prehistoric. Many of the most savage and primitive tribes have knowledge of their use.

In late years the United States has produced about 200,000,000 pounds tannin extract annually and has imported—mainly from South America as quebracho extract—about as much. Much bark as hemlock and oak is also used for the production of leather.

Someone has said that anyone who can make a pot of tea can make a wood extract. In an earlier day this was perhaps so but modern methods have been introduced into this industry.

The most approved practice in the United States is to grind the woods or barks, etc., and extract in a diffusion battery under pressure. This necessitates the use of copper to give the strength and resistance to the acids which are present. Probably the most popular extractor or diffusion cell is about 5 feet diameter and 12 feet long slightly enlarged towards the bottom so as to allow of quick discharge of the exhausted chips. The bottom is hinged and is the diameter of the cell and, on opening, the charge drops out to a conveyor which takes the chips to the boilers for fuel. These usually furnish all the steam necessary for the works. Each wood requires a different temperature and pressure and treatment to get the best extract. Some woods such as quebracho are best extracted by adding some SO_2 to the liquor to dissolve the more refractory tans. Some extracts like logwood are oxidized, the oxidized logwood extract being called "hematine" and this is used for leather dyeing and where oxida-

[1] Ch. Ab., 1913, p. 3835, and C. A., 1907, p. 2635.
[2] U. S. Pat., No. 1032982, Ch. Ab., 1913, p. 2855.
[3] A. G. Little, Trans. Am. Inst. Chem. Eng., Vol. 8, p. 258.
[4] Ch. Ab., 1919, p. 3034, and Ch. Ab., 1917, p. 1295.

tion after applying cannot be used. On the other hand the unoxidized logwood is preferred where bichromate mordants are allowable.

Hemlock—Abies Canadensis.—This was a most important tanning material and is still largely used but unfortunately the eastern supply is diminishing rapidly. Much was used as bark but extracts are now largely substituted. There was an extract works for hemlock in Nova Scotia for a long time and there may be more in other provinces. The Canadian hemlock bark averages from 8% to 10% tannic acid. Unfortunately this is not high as compared with the United States and particularly the western hemlock which has been shown to average 17% tannin.[1] The same authorities show that Penn hemlock averages 13% and Quebec 10.1%.

Other American coniferous woods have been tried but the amount of tannin is much smaller than in the hemlock. The utilization of spruce bark for tans has been mentioned. As this is a useless by-product it may be utilized even though the yield is small.

Oak Bark.—Oak tanned leather is considered the best for harness and belting but perhaps the union tan for sole leather gives the best shoe sole.

All the different woods and tannins differ in containing various other constituents. Some contain glucose which by fermenting, produces an acid liquor which is desirable at certain stages of the process and for certain leathers. Others contain much coloring matter and give colored leathers which are desirable or not according to their purpose. Those extracts which will not ferment such as chestnut and quebracho are used in connection with such fermentable extracts as hemlock, etc., or are used in the latter stages of tanning.

Chestnut Extract.—This is produced in the United States in enormous quantities from the true chestnut tree which produces the American edible chestnut.

A method of drying the extract to a solid by spraying is discussed in Trans. V, 10, p. 421.

The chestnut oak bark is a valuable but entirely separate tanning material.

What seems to be a purely American invention is the production of a tannin from the chipped wood and a soda pulp from the extracted residue, thus utilizing both the fiber and tannin in the wood.

[1] J. Ind. and Eng. Chem., Nov., 1915, p. 915.

The wood must be barked and chipped differently than usual.

What seems to be true of the hemlock seems also true of the chestnut.

Woods grown as far north as New York State seem worthless for tannin. In Pennsylvania they are used successfully but the most prosperous extract works are in the southern Appalachians for example in North Carolina and Tennessee, the southern limit of its growth. Until a generation ago the chestnut tree was considered useless for wood and other purposes but now that it is found useful the blight has struck it and between the tannin factories and the blight it seems doomed to extinction. Whether the European chestnut is immune to the blight is an interesting question and the dendrologists might with profit investigate this with a view of introducing the European tree. Chestnuts, as is well known, are a staple food in Italy.

Dye Woods and Extracts

While the coal tar dye industry languished in America till the war stimulated it the manufacture of dyes from woods was an important industry in the United States in an early day and remained such till the present. Even before the war much logwood extract and much Italian sumac extract were exported to Europe and even Germany was a large customer. Many yellow, blue and black dyes bought from Germany as coal tar colors were composed in great part of American extracts.

Logwood.—While this only flourishes in the tropics yet it is a Mexican, Central American and West Indian Island product exclusively and was unknown till the discovery of America. The United States imports and extracts enormous quantities and the demand during the war was so great that the extract sold for a dollar a pound and the industry expanded greatly. Many of these war babies died soon after the armistice but a larger industry remains for legitimate demand. For the finest broadcloths and like goods where a black with a "bloom" is necessary logwood is still indispensable. As mentioned before, logwood appears either as liquid or solid logwood extract or as "hematine" crystals. The latter are produced by oxidation of the logwood. A favorite method of oxidizing is by blowing air into the extract. Logwood is used for dyeing blues and blacks. Its tin salt is a brilliant purplish red but is not fast and the

same can be said of the aluminum dye or mordant. It requires a mordant, preferably bichromate of potash or a chrome alum to give the fastest dye. With iron it gives a fine black.

Inks are thus made. For leather dyeing a chrome tan acts as mordant to the dye. At the same time the extract is both dye and tan. This makes a particularly good combination for this purpose. Adding a trace of yellow produces a jet black. For weighting silk a tin salt followed by logwood increases the weight to almost any weight that the conscience will allow, although silk weighted moderately is superior in many ways to the pure silk.

In cotton dyeing manufacturers are urged to use logwood in large quantities to give a fast dye and also give weight. The goods are sold by weight and logwood costs less than cotton. In dyeing cotton it is first mordanted with a tan and fixed with tartar emetic or other metallic salt. Then an iron salt is used for the logwood dye which gives a solid black and an increase in weight.

Quercitron or Black Oak Extract.—While this is a tan it is used mostly as a dye. It gives shades of yellow and orange on wool that are quite satisfactory and much used. It takes the place of old fustic and is much cheaper.

It is only found in the United States. A member with experience in this line has stated[1] that 72% of the quercitron extract called flavine was used by the Government during the war as was 80% of the logwood.

Osage Orange.—This is a native American tree found in greatest profusion in the West particularly in Oklahoma and Texas where the best dyewood is found. The tree is used for hedges in the East and as far north as Connecticut, but like all the other dye and tan woods the best yield is from the southern grown woods. Texas and Oklahoma woods are preferred.

It furnishes about 14% of extractible matter and it contains a dye which gives some lemon shades better than quercitron or fustic and gives very satisfactory yellows and oranges on wood. It was used in great quantities for khaki uniforms in conjunction with a little logwood. Like logwood it goes on to a chrome mordant best. It is possible that for leather work this will have a large field as it contains tannin and with a titanium mordant gives a very fine yellow dye. The introduction of this dyewood during the war is due largely

[1] Delaney, C. R., Ch. Ab., 1918, p. 2690, and J. Ind. and Eng. Chem., 1918, p. 796.

to the efforts of the Department of Agriculture who worked on the problem and found its merits as a dyewood.

Previous reference has been made to the work of the Forest Products Laboratory which shows that the barks of pulpwoods contain from 8.35 to 11.34% of tans and that if they were all utilized it should supply 55% of our requirements.[1]

Spent tan bark is of importance in making old Dutch process white lead and tanneries have been erected and run with the primary object of getting a supply of exhausted bark.

A member[2] has pointed out the benefit that the introduction of the chemist has been to the tanning industry.

Wood Distillation

The author was first interested in this industry in 1888 and for many years was solely engaged in erecting and superintending plants having been in Canada for two years during 1898 and 1899 constructing and operating at Fenelon Falls and Deseronto, Ont. the two first retort plants which operated in Canada.

During that time a number of improvements have been introduced in the industry and having contributed some, it is felt that there is justification in bringing them to the attention of the Institute as the Germans, as usual, have rushed in to claim them.

In Trans., Vol. 7, p. 203 is record of paper given at Philadelphia meeting which reviews the industry well as it existed at that time and little has been done of much importance since, notwithstanding the great war call for the products.

It is not believed that any material increase of capacity of plants or improvement of processes resulted from the fevered attempts to immediately increase the volume of product. The paper gives numerous illustrations which show the methods of handling wood and carbonizing it and a few illustrations of crude apparatus used in the older methods of working up and refining the products.

A daily capacity of 4802 cords in the United States and of about 500 cords in Canada was given as the capacity. This would give about 1,500,000 cords as yearly capacity. This should produce about 15,000,000 gallons of alcohol but under the stress of war and present demand the product has not reached this point.

[1] Ch. Ab., 1919, p. 2144.

[2] Teas, J. Ind. and Eng. Chem., 1915, p. 283, Vol. 7.

As little has been said about improved methods of recovering and refining to chemicals it will be discussed here.

As shown in above references the process of carbonizing now largely adopted consists in piling cordwood on an iron car holding 2 cords which is run into an oven retort first developed at Straits, Pa., in 1895. The vapors produced by heating pass to vertical tube condensers and the pyroligneous acid resulting is settled to remove about 15 gallons of tar per cord and the acid liquor passes continuously into pot stills and all but the tar is distilled over. This acid liquor is neutralized with lime and one-third is distilled off to recover the alcohol and the balance is evaporated to dryness to recover the acetate which is dried.

The weak alcoholic product is redistilled in another still to produce 82% which product usually goes to refiners.

The principal reaction taking place in the charring of fiber is the breaking down of the carbohydrate into carbon and water. The reaction is exothermic and with from 14% to 20% of water in the wood the reaction goes on with the application of little heat after action starts. Many attempts to use green wood have failed on account of the impossibility of getting heat into the interior of wood carbonized on the outside. Attempts to regulate temperatures by methods of heating or cooling retorts or of observing them by pyrometers placed at various points outside the wood body are also useless as the exothermic reaction can only be controlled by having the proper amount of moisture in the wood itself where the temperature develops.

A cord of air dried beech, maple or other strictly hard deciduous wood will weigh about 2 tons and there will be produced from it a ton of aqueous pyroligneous acid which contains about 66 pounds of wood alcohol and 132 pounds of volatile acid estimated as acetic. In addition 15 gallons of tar will separate on standing.

To work this by the old process involves distilling a ton of water to remove about 2 gallons of tar. This was not tar when the operation began for by saturating the acid with sodium sulphate a layer of light volatile highly odorous oils will separate and on boiling they polymerize to tars. To distill off the whole body of pyroligneous acid, then to distill off one-third after neutralizing to reclaim alcohol and evaporate the residue for acetate means a double evaporation of 1 ton or an evaporation of 2 tons of water. To economize on this immense expenditure of fuel necessary the author devised an improved process.

Improvements in Producing Chemicals from Wood Distillation

In 1906 two patents Nos. 824906 and 835501 and in 1908 patent No. 896434 were granted to the writer, the application date going back to December, 1904.

They embrace a process of distilling wood alcohol directly from crude pyroligneous acid in about 24% strength, evaporating the residual acid in multiple effect evaporators which also concentrate the acetate and the apparatus is disclosed and claimed. At this time the universal process used in wood distillation works were those previously described above. There was not in any wood distilling works a continuous column still nor any column still working on anything except for refining 80% alcohol and all the installations of these latter were put in by the author or followed those patterns. There was no installation of multiple effect evaporation whatever or any vacuum apparatus used nor was any exhaust steam used for any boiling work.

To remove the alcohol directly from the pyroligneous acid in any column still or any apparatus which would yield 25% alcohol had never been done before in the United States or described elsewhere. The patented process was worked by using a continuous still of the type known as " beer " stills as used in distilleries but on account of the tar many modifications had to be made and it took four months' work after installation to get into successful operation. To avoid diluting the acid residue with water from condensed steam a boiler or " superheater " was attached.

This had never been done in the grain industry but was afterward extensively adopted there. The raw cold crude acid was continuously pumped in at the top and a distillate of about 25% alcohol was made. It would have been easy to have made 80% or 90% alcohol as is done in the grain alcohol industry but at this point many oily impurities will separate out which will not separate out in higher or weaker strengths. After removing these by settling it was found that by the addition of an excess of alkali that a number of aldehydes and ketones would polymerize and form "bakelite" with the phenols as creosotes, etc.

On distilling the thus purified liquid it yielded on redistillation in a similar still an 80% or 90% alcohol so free from oils that it was perfectly miscible with water as were all the subsequent distilled fractions.

On addition of such alkalies as lime to pyroligneous liquor a series of color reactions take place. At first the light straw colored liquid

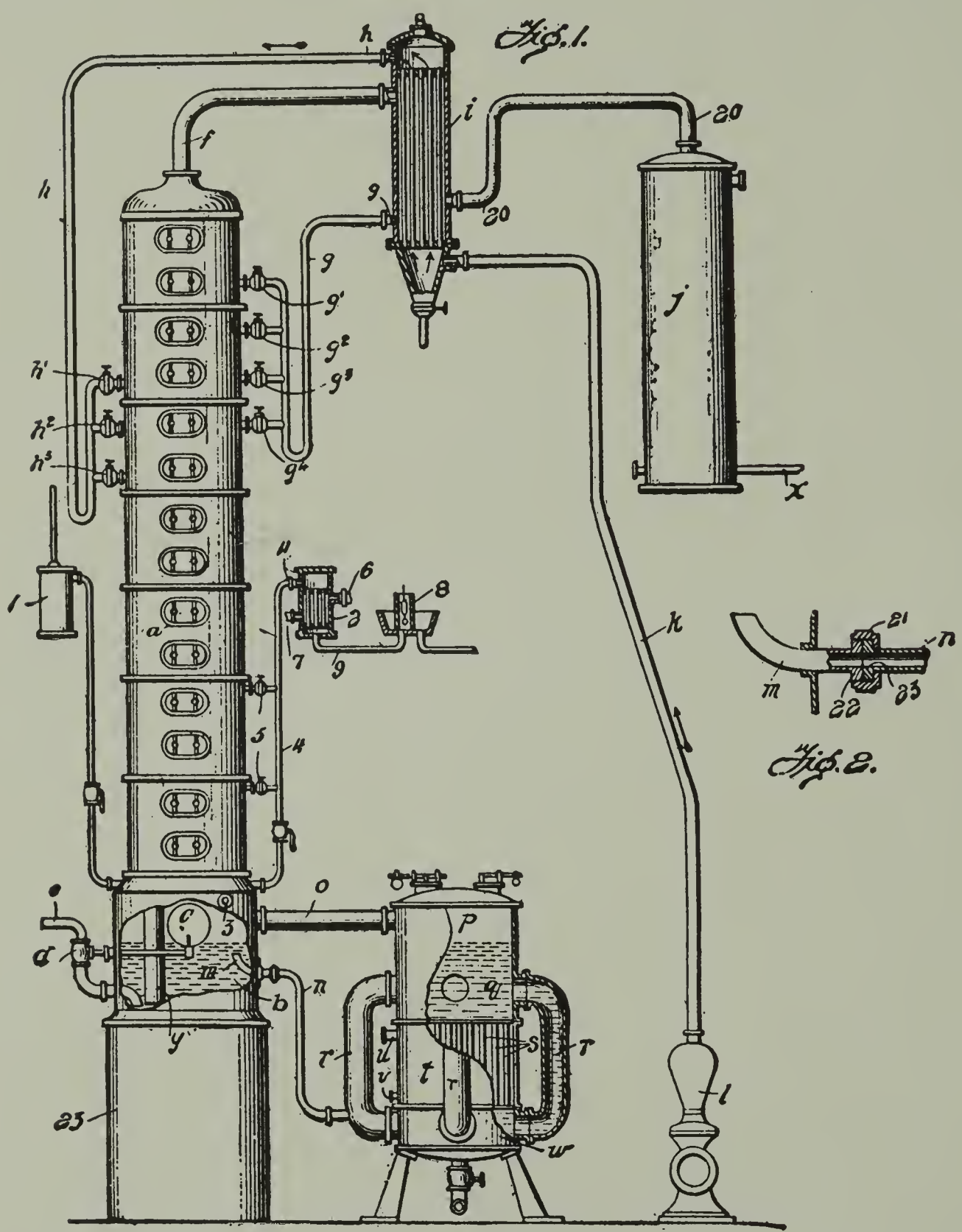

FIG. 1.—Distillation Apparatus. U. S. Patent No. 896484.

turns darker and greenish, then it turns a red which if strong is a deep purplish wine color.

At this point it is neutral. This is the point at which neutralizations had previously stopped. But with 25% this distillate from

which nearly all the acid was removed and as the acetate was to be made from the other portion it was advantageous to add excess of lime. No one had previously recognized the importance of separating oils from an acid distillate of about 25% alcohol nor of then adding excess of lime to polymerize alkali-sensitive impurities to produce perfectly miscible 80% crude. Many to-day do not recognize it and have produced 80% crude which defied purification to an extent necessary for making formaldehyde or dyes or other chemical purposes.

A somewhat long description has been given but not as long as the lawsuit which has been pending for eleven years and though all decisions have been in favor of the patent the collection of damages still remains for settlement

It may be said that nearly all the large plants in the West promptly put in infringing plants but by appealing to the law they settled under duress.

It may be remarked here that the author never found any so-called business man who would recognize any intellectual property whether covered by patent or not unless compensation was forced by court mandate.

The acetate process illustrated here co-ordinated with the alcohol process uses the acid from which the alcohol has been removed. This hot pyroligneous acid containing about 6% acetic acid, 4% impurities forming tar and 90% water is placed in the first vessel No. 18, of a multiple effect evaporator. All parts coming in contact with the acid or its vapors must be of copper. The acid liquor was distilled in the first installation at Ashland, Wis., by the exhaust steam of the furnace blowing engine, introduced at No. 19.

The acid vapors went through pipe No. 22 to the "calendar" of the second effect, or its heating chamber, and were condensed there. The purified acid liquid was taken out and neutralized with lime in tub 27, as in the old way described. The neutralized liquor was run into the second effect, No. 24, through 28, and was evaporated by the heat of the condensing acid vapors. Thus, the acid was distilled and purified and the acetate concentrated to the crystallizing point using only exhaust and waste steam. This process made the manufacture of gray acetate of lime profitable in the Lake Superior region where there were blast furnaces. Previous to that time most of the acid liquor was wasted as it was said to be impossible to evaporate it at profit on account of the fuel necessary. The Pennsylvania

plants had natural gas for the work and they considered fuel as worth nothing then.

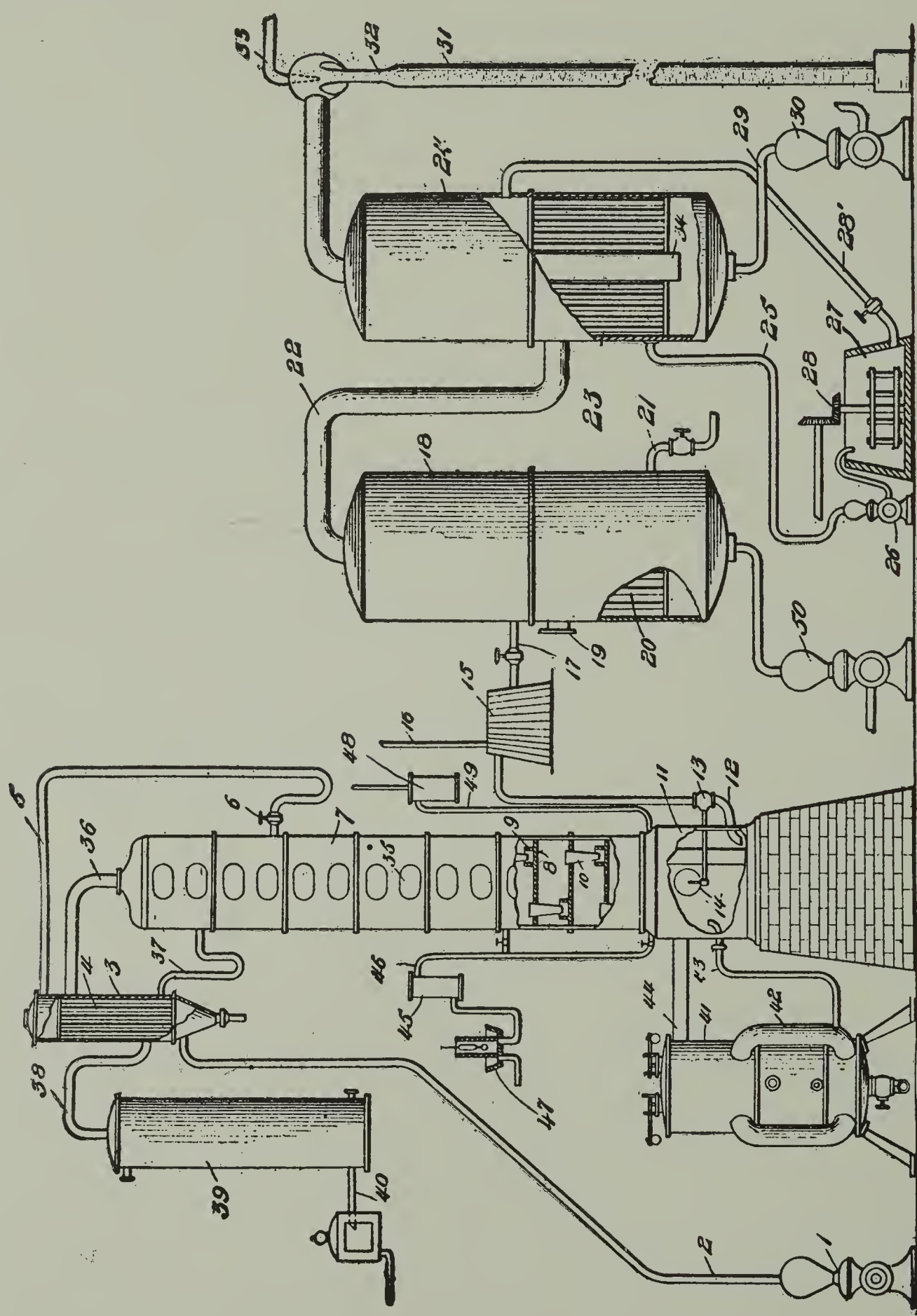

FIG. 2.—Process of Making Acetates. U. S. Patent No. 835501.

The advantages of the combined processes above are, first that by removing the alcohol before attempting to put the liquid into a mul-

tiple effect vacuum evaporator that the high vapor pressure of alcohol does not interfere with the operation of the apparatus under vacuum. 2d. The intermediate treatments of the alcohol produce a better refined article than can be made otherwise and the process is much more economical of fuel. By putting the acid liquor into the first apparatus and the neutralized liquor into the second only one of the vessels needs be of copper and the water from the sccond may be sent to waste and a jet condenser used. Broadly speaking it may be said that the introduction of the continuous still and the multiple effect evaporator has doubled the production of alcohol and acetate.

Later some apparatus to crystallize acetate and dry it has been introduced. The most important and novel apparatus is a woven wire mattress like belt which picks up the concentrated acetate in the meshes and carries it through a heated chamber and at the end the dried and agglomerated acetate is knocked off in little chunks. Another process uses the roll drier to partially dry the acetate which is then finished in a rotary drier. It is the author's experience that with proper skill acetate may be crystallized satisfactory in the ordinary double bottom pans or pans with pipes in them. This may then be thrown into a rotary drier. Rotary driers were introduced successfully in 1900 for acetate but attempts to use them as evaporators led to their final discard.

The statement has been put forth that the removal of the alcohol by pre-distillation from the acid leads to loss of acid in the distillate but it is evident that any acetate in the residual liquor from the alcohol distillation may be evaporated and the acetate recovered. The water present in the alcoholic distillate was in the original pyroligneous acid and separating it into two portions does not change its volume.

Rectification of Crude 80% Wood Alcohol

Wood alcohol is bought and sold and gauged on the Tralles scale which reads percents by volume of grain alcohol. It is accurate for wood alcohol at 60° F. and at 99% but not at other temperatures and strengths. The Gay-Lussac scale is the same graduated at 59° F. The presence of oils or aldehydes, etc., dissolved in the crude, of course, interferes with the correct reading of the alcoholic contents.

The 80% crude alcohol made under the old processes or any process other than that described above is a pretty crude liquid

usually containing oils in solution that will precipitate on diluting. It also contains about 25% of impurities eliminated in the heads as they are more volatile than alcohol. They comprise acetone, acetaldehyde, and formaldehyde and oils. This mixture when separated and purified by distillation and treatment with acids and alkali is known as "methyl-acetone." The tails furnish methyl-ethyl ketone now on the market and some other oils which have such a rank odor they are not used. About $\frac{1}{10}$ gallon per cord of allyl aclohol has been made.

In eliminating the impurities the heads or the fore-runnings form what is sold under the name of " methyl acetone " a mixture of methyl acetate 40%, acetone 40% and methyl alcohol 20%. This has a specific gravity the same as 80% alcohol.

Methyl acetone has a constant boiling point of 55° C. and can be distilled over caustic soda with very little decomposition. By refluxing or superheating acetate of soda is formed and methyl alcohol comes off.

Though by iodine test it forms iodoform indicating acetone and the acetate indicates esters it has different physical and chemical characteristics from a synthetic mixture of the pure products as above. For one thing it has none of the characteristic smell of acetone nor the fragrant smell of methyl acetate. The writer has never seen a barrel of pure acetone or methyl acetate known to be produced from this product though small samples are reported to have been separated. During the famine of acetone in war times with the fate of nations hanging on acetone no one produced an acetone from alcohol heads suitable for cordite. Though perhaps some methyl acetone was used in desperation it was never confused with the pure article from decomposition of acetate nor did it work as well. It is a better solvent of many gums, resins, cellulose esters and some other things than the synthetic mixture. For chemical works making formaldehyde and di-methyl aniline and other compounds methyl alcohol is produced in large quantities 99% pure and with less than 0.10% acetone and remaining undiscolored on addition of permanganate and with caustic dissolved in it.

Acetate of Lime

The old method of making acetate was by neutralizing crude undistilled pyroligneous acid producing brown acetate of 60%

purity. With HCl this makes a very satisfactory acetic acid and it produces an acetone with more higher ketone oils but intumescence takes place to such an extent that its destructive distillation is troublesome.

Sulphuric acid acts on it with great decomposition producing much SO_2 when acid is made from it but with the prospects of increase in HCl in the future as a by-product of chlorination of organic compounds and in other residues perhaps the brown acetate will come back.

The gray acetate is made by neutralizing with lime the distilled pyroligneous acid and shows 80% purity on estimating acetic acid.

What the other 20% is the author does not know and knows no one who does.

Acetic Acid

The older process of making acetic acid was to distill gray acetate with sulphuric acid in a still [1] of cast iron and flat bottom set over a fireplace with copper neck leading to copper condenser. The still had a removable section at bottom to one side and the residual calcium sulphate was thus removed.

SO_2 and weak acid come over at first and the acid gets stronger till the still is nearly dry when steam or water must be added to remove the last portions. The crude acids of varying strengths according to the time taken and amount of water added are re-distilled. A wooden still with a stoneware column or condenser is used but a copper distilling column is better.

The crude acid distillates are separated according to strength and amount of impurities such as SO_2 and pyrogenic matter, etc. After distilling a portion and evolving SO_2, permanganate or bichromate is added till no further immediate action takes place; the residual distillation is for stronger and purer grades.

The distillation of the stronger acid is done in copper stills with columns and stoneware and glass have been substituted with some little success.

On distilling a solution of acetic acid of all moderate strengths in an ordinary flask the distillate will contain one-half the strength acid as the residue from which it was produced. Thus, there is, with any fractional distillation, a constantly stronger distillate till

[1] U. S. Pat. No. 535553 and 608019.

finally the residue, and consequently the distillate is glacial. The last stages are difficult and are best performed in glass. The rectification is best performed in a copper still and column. Vacuum stills have been introduced in late years but are not of importance.

The commercial grades are No. 8 which is 28%, and 60% and 80% waterwhite which will stand permanganate without discoloring and pure glacial of 99%+.

100 grain vinegar is 10% acetic acid.

Until the war stimulated production all acetic acid except vinegar was produced from distilling acetate of lime from wood distillation.

During the war acetone production led to processes making acetates and acetone. The most important we will see at Shawinegan where glacial acetic acid is made from carbide and for the glacial grade it promises to be a prominent factor in the market. It must be remembered that before the war acetate sold at $1.50 per hundred making the acid contained worth 2.5 cents per pound, now with acetate at 3.5 cents it would be worth 6 cents a pound. But with the present price of alcohol, acetate will be sacrificed at any price and 3-cent glacial acid is possible from wood distillation, though it is hoped it will not be necessary.

Through double decomposition of calcium acetate with sodium sulphate a cheap acetate of soda can be made which with chlorine and sulphur chloride will make a rather cheap anhydride if commercial processes are developed to use it on a large scale.

Acetone

Acetone is made from destructive distillation of lime acetate in three different forms of apparatus. The first apparatus is like the acetic acid still described as the apparatus was originally patented for acetone manufacture.[1]

A large amount of acetone was made during the war with this apparatus and better yields and general results claimed than by other processes. The users of the other processes make the same claims.

The second process uses a rotating cylindrical retort with charging door and discharge in rear and in front trunnion is an escape for acetone vapors and gases which go to a condenser. Where natural gas is available these retorts give good results.

The third process was introduced by the Germans and consists

[1] U. S. Pats. Nos. 535553 and 608019.

of a retort and car exactly like the United States oven retort system and could be made by using the drawings for these and was probably so made after a visit of German wood distillation experts to the United States. The car has pans on it which were filled with acetate and rolled into the retort and distilled just as the wood is distilled. During the war no American wood distiller could be induced to use his oven retorts for making acetone so badly needed. Though these are somewhat larger and the charge would probably take longer there appears no reason why they would not function perfectly. The old round retorts are also well adapted to making acetone by putting in pans of the right shape to fit. None of these were used, however, though some were idle. There was therefore no necessity of constructing the large acetone plants built during the war which are now idle and useless. If we had more standard retorts more alcohol could now be made to supply the demand.

Competitive Processes

The war has not resulted in any materially greater capacity of wood distillation plants but has resulted in bringing out other processes of making acetone and acetates. A large installation near Baltimore distilled molasses and made vinegar or acetic acid from the alcohol by the old standard methods long practiced at many places in the United States. The acid was neutralized with lime and evaporated and destructively distilled for acetone using the standard rotary retort before described. Though there is no new step whatever except neutralizing acetic produced from fermentation instead of by wood distillation the plant did not seem to work for several years well until one of our members took hold and fired the German management.

No acetates or acetone has been made by this process since the armistice.

The production of acetone from soda waste liquor has been mentioned but none has appeared on the market.

At Shawinegan Falls we may see the acetone plant which now has historical interest only as none has been produced for commercial work.

At San Diego the author had the pleasure of examining the very interesting process of fermenting seaweed to acetic and other organic acids and described it in Vol. 10, Trans. It was a very attractive

process but closed down immediately the armistice was declared. It made acetone as one product while potash was saved.

The Fernbach process of fermenting starch to normal butyl alcohol and acetone was developed at Toronto and at other places and at Terre Haute it is being started again and will produce considerable acetone as by-product. The demand for fusel oil made scarce by prohibition results in the old distilleries being re-started up to make the butyl alcohol substitute.

It thus appears that while the market for wood alcohol seems attractive that competition may appear on acid and acetone.

Wood Tar

About 15 gallons of tar are produced per cord of wood distilled. Most of this is burned under boilers though some oils are produced from which a little beech wood creosote is made and some is used in flotation of ores. The Forest Products Laboratory of Canada has investigated the wood oils for flotation of Cobalt ores and finds generally that by using twice as much hard wood oils as is necessary with pine oils that about as good results may be obtained.

No research work on American hard wood tar has ever been done or published and it is impossible to find any record of an analysis that is in any way complete or that will tell the substances contained in it and their proportion. There are a lot of statements that certain investigators have detected various chemical compounds in it; but whether they were traces or whether they comprised substantial amounts of the product is not stated.

Most of the published work refers to European tars produced from different species of trees than are used in the United States and Canada.

Charcoal

As is well known charcoal was one of the most ancient fuels for one of our ancestors who had come down from the trees found that fire was a friend instead of an enemy as all other animals thought. When he made use of fire he performed the primary feat that lifted us above the lower animals. Charcoal was the product of incomplete combustion and while glowing served to carry fire to the cave where needed. The first artist who preceded the Neanderthal man used charcoal for crayon. As much charcoal iron is made in America

to-day as ever but the vast increase in coke iron has made us forgetful of this.

A large amount of charcoal is used for domestic purposes, particularly in Canada.

The properties of charcoal in absorbing gases and decolorizing liquids were long known. Under direction of Col. Dunn experiments were conducted some years ago that proved that charcoal from rotten wood will, if slightly wetted, and a slow current of air is passed through it, ignite and burn and this accounts for many cases of spontaneous combustion in charcoal cars.

In the obsolete process of making American whiskey it was customary to filter the 50% alcohol through charcoal and this was specially treated to activate it. Hard wood charcoal produced by the ordinary retort process was placed in a stone or brick kiln and ignited and burned till about 24% was consumed. This produced a very high temperature and the tar was thus burnt and steam might then be run in and the kiln closed till it cooled off.

This produced a coal probably as well activated as any that went into gas masks. It must be remembered that the Germans had nothing but hard wood charcoal for gas masks but it was found to be remarkably efficient.

The Correlation of Forest Industries with Dendro-chemistry

The chemical industries of the forest here described are all being worked at various places but in too many cases they are not pursued as by-product industries. The tendency of the American is to go in for big plants and rapid production without regard to economy of raw materials which did very well when our resources were seemingly unlimited but that time is rapidly passing for all and has passed for many to their sorrow.

The ideal forestry operation is one where every species of wood is taken and every part is utilized for making chemicals or for producing heat if it is unsuitable to more profitable use. Every sawmill has potentialities in its wastes as material for chemical products and as fuel for chemical industries. When these are utilized there will be greater profits in the forest and it will furnish more useful products and part will be conserved for posterity.

ADSORPTION BY SILICA GEL
THEORY AND APPLICATIONS

By E. B. MILLER

Read at the Montreal Meeting, June 29, 1920

Theory

The adsorption of gases and vapors by certain porous bodies such as charcoal, kieselguhr, etc., has long been a matter of common knowledge. It was soon found that the retention of gases and vapors by such adsorbents was not related to the chemical composition of the substance adsorbed, but was in some way connected with the ease of condensation of the absorded gas or vapor. A rough parallelism was noted between the adsorption of a gas and the boiling point of the gas when condensed to a liquid.

Much of the uncertainty and inaccuracy of the early adsorption work was due to the difficulty of preparing adsorbents of constant properties. When it was found that adsorbents could be prepared from certain colloidal solutions in an easily reproducible manner, it then became possible to study the phenomenon of adsorption with some degree of certainty. Furthermore, when it was found that these latter adsorbents possessed the power of adsorption equal if not superior to that exhibited by adsorbent charcoal, the experimental study was made comparatively simple.

Silica gel, prepared from the coagulation of a colloidal solution of silicic acid, is such an adsorbent, and in many respects is an ideal substance for the study of adsorption. It is easily made under conditions that may be reproduced with considerable exactness. It is prepared from inexpensive raw materials, water glass, and either hydrochloric or sulphuric acid. Chemically, it is most inert and is therefore stable in air even at high temperatures.

The adsorption of a number of gases by silica gel has been studied at different temperatures.

From the results of such experiments it has been possible to discover the factors that are of importance in determining the extent of adsorption.

It was found that vapors of liquids of a high boiling point were more strongly adsorbed than vapors from a liquid of a low boiling point. Furthermore, adsorption decreased with increasing temperatures. Also, the greater the partial pressure of vapor being adsorbed, the greater was the extent of the adsorption. All these facts suggested the idea of condensation of the vapor in the adsorbent. Pursuing this thought we selected as a measure of the ease of condensation the ratio of the pressure of the vapor in equilibrium with the adsorbent to the vapor pressure of the liquid at the temperature of adsorption. This ratio is herein designated as the "corresponding" pressure. It was soon established that vapors of high corresponding pressure were more strongly adsorbed than those of lower corresponding pressure. The relationship while qualitatively true did not correctly represent the phenomena quantitatively.

It was then noted that when the corresponding pressure equaled unity, i.e., when adsorption was measured at the vapor pressure of the liquid, the volumes of the adsorbed liquid were in all cases the same. In other words, it is advantageous, inasmuch as it tends towards simplicity, to express adsorption in terms of volume of adsorbed liquid rather than in weight. The volume of adsorbed liquid was obtained by dividing the weight of the substance adsorbed by the density of the liquid at the temperature of adsorption.

This simple relationship was found to be true only in the case of measurements carried out at a "corresponding pressure" of unity. At lower "corresponding pressures" the volume of the adsorbed liquid was not the same at the same "corresponding pressure." This discrepancy was attributed to the fact that the condensed liquid under "corresponding pressures" less than unity had a density smaller than the normal density. Furthermore, the greater the compressibility of the liquid the greater was the deviation of the density of the liquid in the adsorbent from the normal density. By taking these additional facts into consideration all of our experimental observations were quantitatively brought into complete harmony. We are therefore in position to say that the factors influencing adsorption are the corresponding pressure and the compressibility of the adsorbed liquid.

We have yet to consider the properties of the adsorbent that

determine its activity. Inasmuch as the chemical nature of the latter apparently is of no moment, we are forced again to a consideration of a physical property. All adsorbents are porous, and the internal volume is large and composed of exceedingly fine pores. Furthermore, capillarity tells us that a liquid in a small tube possesses a lower vapor pressure than the normal vapor pressure. In other words, it is easier to condense a vapor into a small capillary than on to a level surface. We have therefore in the above all that is necessary to characterize an adsorbent. It must possess as large an internal volume as possible and this volume must be made up of spaces of minimum dimension.

When we consider silica gel as an adsorbent for the vapor of a liquid at a given temperature, we have to take into account two things: 1, the partial pressure or concentration of the vapor to be adsorbed; and 2, its vapor pressure at the temperature of adsorption. Denoting the partial pressure by P and the vapor pressure by Po, we may define the "corresponding pressure" by the quotient $\frac{P}{Po}$. It has been found experimentally that the amount of a particular vapor adsorbed increased with increasing value of the ratio $\frac{P}{Po}$. Now for a given partial pressure, the value of $\frac{P}{Po}$ increases with decreasing temperature, and for a given temperature, the ratio $\frac{P}{Po}$ increases with the increase of partial pressure. Hence in practice, we have better adsorption the lower the temperature and the greater the concentration of the vapor to be adsorbed. Maximum adsorption, at a given temperature, will take place when $\frac{P}{Po}$ has its maximum value, which is unity.

Let us consider a few examples. We may adsorb water vapor at 30° C. from air saturated at 30° C. Under these conditions, $P = Po = 30$ mm., and the gel will take up an amount of water corresponding to 25 to 27% of its own weight.

If we consider a similar mixture of sulphur dioxide and air at 30° C., that is, a mixture in which the partial pressure of sulphur dioxide is 30 mm. (which corresponds to about 4% by volume) the ratio $\frac{P}{Po}$ is much smaller than in the case of water, due to the

greater vapor pressure of sulphur dioxide. From such a mixture the gel takes up sulphur dioxide to about 6% of its own weight.

If we use a mixture of carbon dioxide and air of the same concentration as above, the value of $\frac{P}{Po}$ at 30° C. is quite small and only a slight amount of carbon dioxide will be adsorbed. For the permanent gases the ratio at 30° C., is extremely small and hence in all the above cases the adsorption of air is negligible.

The effect of temperature is shown by the following: From a mixture of sulphur dioxide and air containing 4% by volume of sulphur dioxide (partial pressure about 30 mm.), the gel takes up 4%, 6%, 8.2% and 11.1% sulphur dioxide by weight at 40°, 30°, 20° and 10° C., respectively. The effect of concentration may be illustrated by the following: Working at 30° C., the gel takes up 2.3%, 6%, 7.1% and 8% by weight of sulphur dioxide from mixtures containing 1%, 4%, 6% and 8%, respectively.

Inasmuch as the adsorptive power of silica gel does not depend upon any specific chemical action, but rather upon the physical properties of the vapor to be adsorbed, it may be used successfully at ordinary temperatures and atmospheric pressure to remove from air the vapors of any liquid mixed with air in any proportions, provided the liquid boils under atmospheric pressure, above −10° C. We must exclude, of course, any vapor which like hydrofluoric acid attacks silica.

From what has been said it will be obvious that lower boiling liquids may also be adsorbed, but it would hardly be practicable to do so efficiently at the ordinary temperature. Even the so-called permanent gases may be adsorbed at low temperatures, and it is quite likely that such a problem as the fractionation of liquid air into oxygen and nitrogen would be made easier by the use of silica gel.

From what was said above in the discussion of corresponding pressure the obvious procedure to follow in order to recover the adsorbed material consists in two steps: 1, raise the temperature, and 2, decrease the partial pressure of the vapor over the gel by evacuation or by displacement with air, steam or other vapor.

Thus absorbed water may be driven out by air at 115° C., more rapidly at 125° C., and still more rapidly at 150° C. High boiling liquids may be adsorbed without difficulty, but require a correspondingly high temperature for recovery from the gel. Silica gel is almost ideally adapted to the adsorption and recovery of the vapors

of liquids boiling between 30° C. and 150° C. in that it takes up large quantities of these vapors at room temperature and gives them up readily at slightly elevated temperatures, that is, from 100° C. to 200° C. This classification includes most of the important solvents, such as ether, acetone, methyl and ethyl alcohol, benzene, gasoline, methyl and ethyl acetates, and many others. We shall see also that it offers a satisfactory means for drying air and for the recovery and concentration of the vapors of more volatile liquids such as sulphur dioxide.

A more detailed discussion of the theory of adsorption as applied to sulphur dioxide may be found in an article by John McGavack, Jr., and W. A. Patrick, in the Journal of the American Chemical Society 42, 946 (May, 1920).

LABORATORY RESULTS

Experimental Work. We give herewith some experimental results, obtained on the laboratory scale, on the adsorption and recovery of the vapors of five typical substances:

These are

1. Sulphur dioxide, boiling point..... − 8° C.
2. Ether " " ..... + 35° C.
3. Acetone " " ..... + 56° C.
4. Benzene " " ..... + 80° C.
5. Water " " ..... +100° C.

We also give some data on the use of gel in recovering the vapors of

6. Gasoline.

We will consider these in the order named.

Sulphur Dioxide

Adsorption. The adsorption of sulphur dioxide by silica gel has been thoroughly studied both by the static and dynamic methods.

The static method consists in placing a convenient amount of the gel in a small apparatus which is then exhausted to the highest vacuum obtainable. To insure complete removal of air the vessel is heated to 300° C., and this temperature maintained, with the pump in continuous operation, for six hours, or until no more air can be pumped off. The pump used is the Gaeda high vacuum mercury pump.

The vessel containing gel is then placed in a thermostat and a known amount of sulphur dioxide introduced. After the system has come to equilibrium, which requires not over fifteen minutes, the pressure is observed and the quantity of sulphur dioxide adsorbed determined. Figure 1 gives the results of four series of results obtained in this way

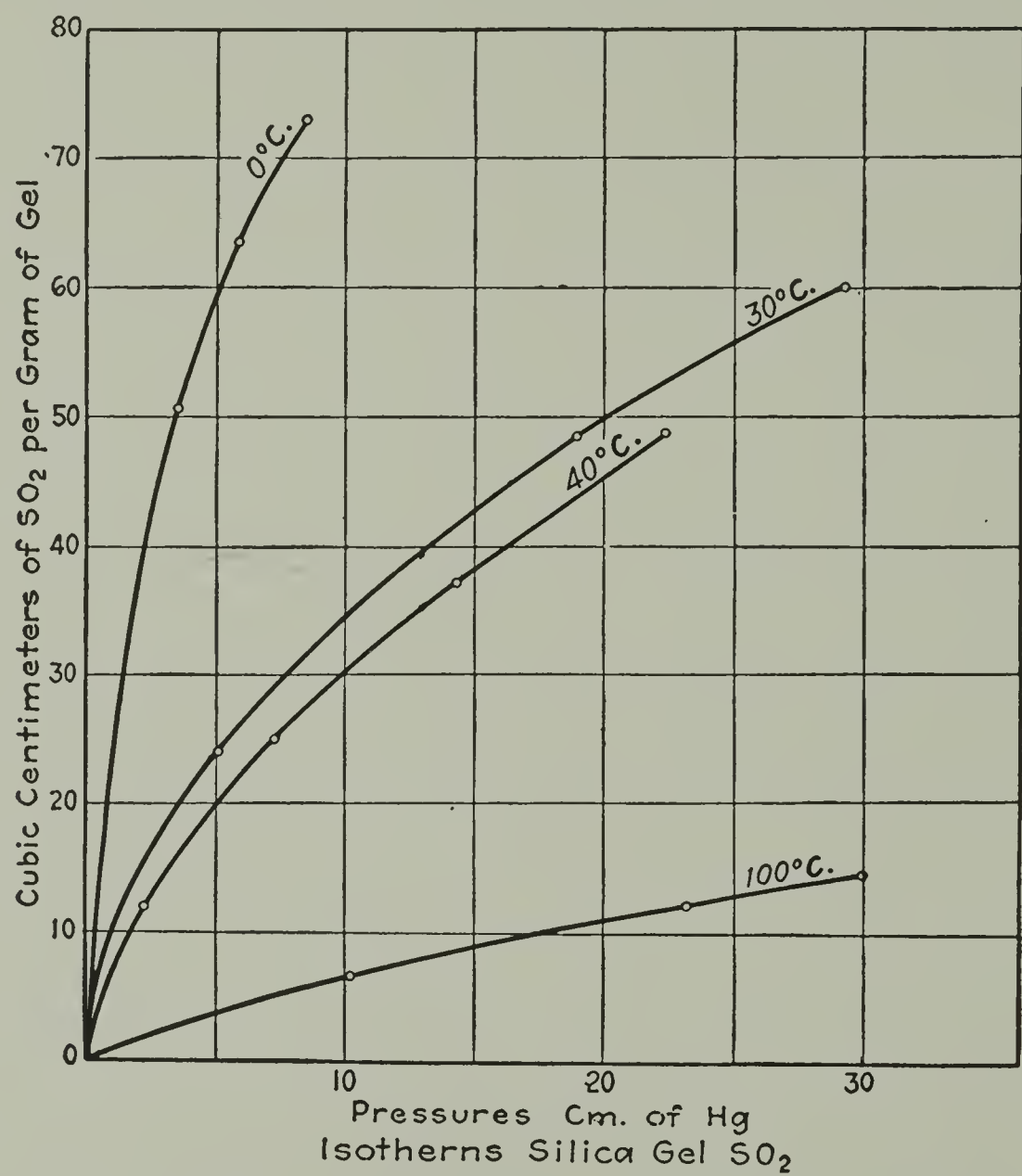

FIG. 1.—Adsorption of SO_2 in c.c. at 0°, 30°, 40°, and 100° C.

at 0°, 30°, 40° and 100° C., respectively. Figure 2 gives a recalculation of these results in which the ordinates express the adsorbed sulphur dioxide as per cent of gel weight, instead of cubic centimeters per gram of gel.

The dynamic method consists in placing a convenient quantity of granular gel, usually 10 gm., in a glass tube of 1 to 2 sq. cm. in section, bent in the form of a U for convenience of immersion in the thermostat, and passing through the gel at a given temperature a definite mixture of sulphur dioxide and air. The air and sulphur dioxide

are metered separately through carefully calibrated flowmeters similar to those used by the Chemical Warfare service, passing first into a

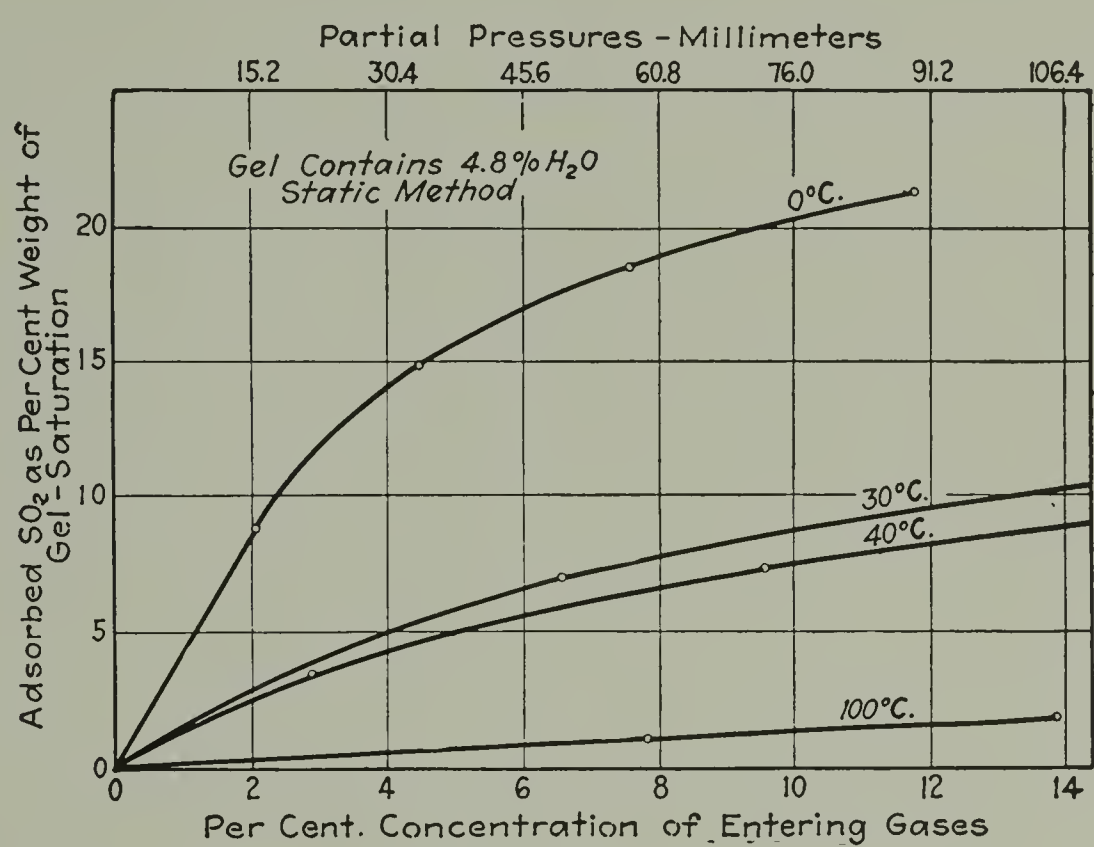

FIG. 2.—Adsorption of SO_2 in Per Cent of Gel Weight.

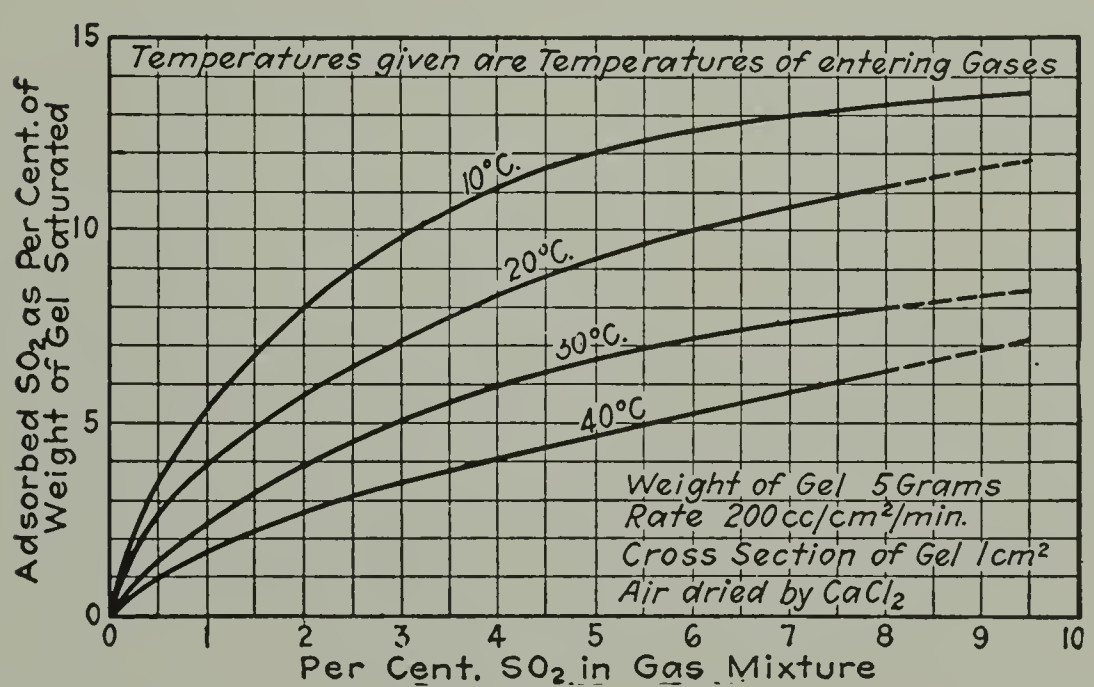

FIG. 3.—Adsorption of SO_2 in Per Cent of Saturated Gel Weight.

mixing chamber and thence over the gel. Under these conditions the gel adsorbs the sulphur dioxide completely for a certain period. At the end of this period a trace of gas begins to come through, the

percentage of sulphur dioxide in the exit gas increasing rapidly, becoming finally equal to that of the entering gas. This corresponds to the point of saturation for this particular mixture and temperature.

The results of a series of experiments in which the concentration of the sulphur dioxide-air mixture varied from 0.5% to 8% by volume and the temperature varied from 10° C. to 40° C. are given in Fig. 3. A comparison of Figs. 2 and 3 shows substantial agreement between the results given by the two methods. In other

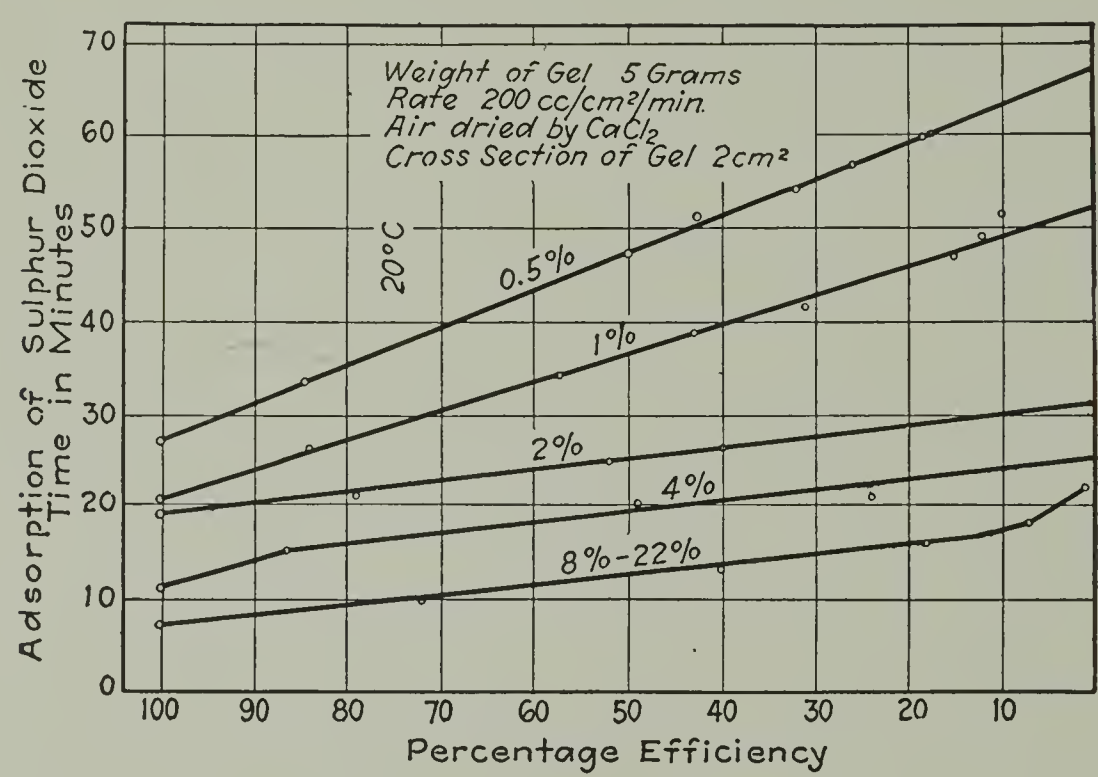

FIG. 4.—Percentage Adsorption Efficiency.

words, the presence of a permanent gas has, for commercial purposes, a negligible effect upon the adsorption of sulphur dioxide by silica gel.

The details of one set of experiments (at 20° C.) are shown in Fig. 4, in which the results are shown as percentage efficiencies against time. The ordinates here express the sulphur dioxide adsorbed as percentage of the total being admitted to the gel. With regard to these experiments we desire to make the following comments.

1. The rate of flow of gas through the gel was 40 c.c. per minute per gram of gel or 0.65 cubic foot per minute per pound of gel. This means that the time of contact of gas with gel was approximately 0.8 second.

2. Notwithstanding this short interval allowed for adsorption, in each run no detectable trace of sulphur dioxide passed the gel for a considerable period. In other words, we had 100% adsorption

for a certain period, depending upon the concentration, after which the efficiency curve falls off abruptly to zero adsorption. We denote the time at which the first trace of sulphur dioxide comes through as the "break point." An examination of the curves at 20° C. will show that for all concentrations the gel was not less than 57% saturated at the break point.

3. As already stated the rate used in these experiments was 40 c.c. per minute per gram of gel, which allows about 0.8 second for contact. If necessary, higher rates may be employed. Reference to Fig. 5 shows that for a 0.75% gas the slopes of the efficiency curves are very nearly the same for rates ranging from 25 c.c. to 75 c.c. per minute per gram of gel. A practical rate for adsorption in general

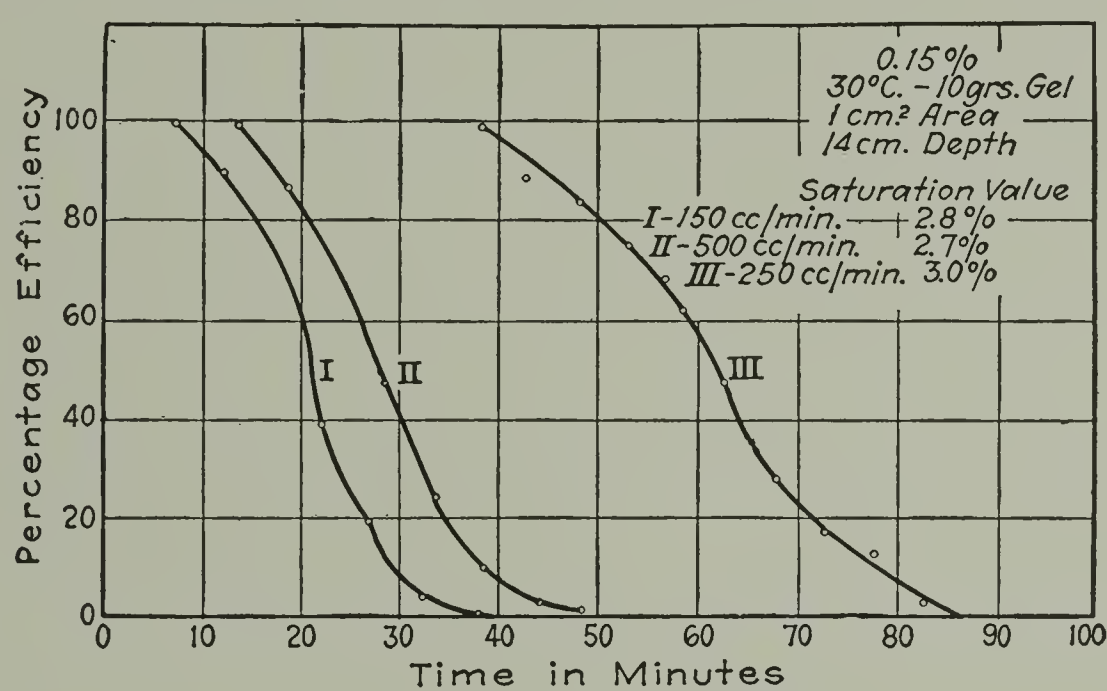

FIG. 5.—Comparison of Efficiency.

is 50 c.c. per minute per gram of gel., which is approximately 0.8 cubic foot per minute per pound of gel. This allows about 0.6 second for contact.

The gel granules used in all these experiments varied in size between 8 and 14 mesh. The size of the gel particles has a very practical bearing in two respects. In the first place it is obvious that the larger the particles the greater the time necessary for the adsorbed material to penetrate to the interior and that, for adsorption purposes, it would be desirable to reduce the size of particles as much as practicable. The final saturation value would not be changed, but the break point would occur later and the latter part of the efficiency curve would be steeper, which is advantageous. Clearly, however, for the type of absorber being considered, there is a

practical limit to the size of particles that may be employed, for it is obvious that the smaller the size the greater will be the pressure required to force the gases through the gel bed. Resistance to gas flow will be discussed further under the head of "Plant Results."

Recovery. With respect to the recovery of adsorbed material, silica gel has marked advantages over other adsorbents. By reference to the curves already given it will be seen that the gel takes up very little sulphur dioxide at 100° C., even with high concentration of gas. These curves indicate the obvious procedure to follow in using the gel. Adsorption should take place at as low a temperature as is practical and for recovery the whole should be heated to 100 °C. or more. The exact procedure to be used depends upon the concentration of sulphur dioxide desired.

Let us assume for example that we have a gas which is 4% sulphur dioxide by volume, and that we wish to concentrate this to 8% for use in the lead chamber process for making sulphuric acid. And let us assume an adsorption temperature of 30° C. We see from the curves that using a 4% gas and working at this temperature, the gel will take up 6% of its own weight of sulphur dioxide. After adsorption the temperature is raised to 100° C. and the sulphur dioxide swept out by means of an air stream, the volume of air being so regulated to give the desired concentration. We may, if it is so desired, obtain in this way a much higher concentration than 8%. It is possible to go from 4% to 30% in one step by simple air displacement at atmospheric pressure. It is easily possible in this way to concentrate as lean a gas as 1% to 8% in one step.

If the object is to obtain a very high percentage gas, as for example in making liquid sulphur dioxide, air would not be used, but the adsorbed gas liberated at 100° C. or above, by evacuation. By proper regulation of temperature, pressure and volume of air admitted, any desired concentration up to practically 100% may be obtained.

Solvent Recovery

Considerable losses of valuable solvents such as ether, acetone, alcohol, benzene, etc., occur in a variety of industrial processes. In the recovery of such solvents silica gel will probably find some of its most important applications. The general principles already discussed apply in this field and we can predict approximately the adsorptive power of the gel for the vapor of a particular solvent before determining it experimentally. These general principles

have already been illustrated in some detail by experimental data on sulphur dioxide, and it will not be necessary to go into the same detail hereafter.

For the recovery of solvents after they have been adsorbed by the gel, the most satisfactory method, applicable in nearly all cases, consists in heating the gel to the proper temperature and sending steam directly through it. For the volatile solvents here considered 105° C. is sufficient to bring about rapid distillation from the gel. This method is particularly adapted to the recovery of substances which, like ether, benzene, etc., are but slightly soluble in water and do not react chemically with it.

Steam displacement was used in the laboratory experiments described below. In carrying out an experiment the tube contain-

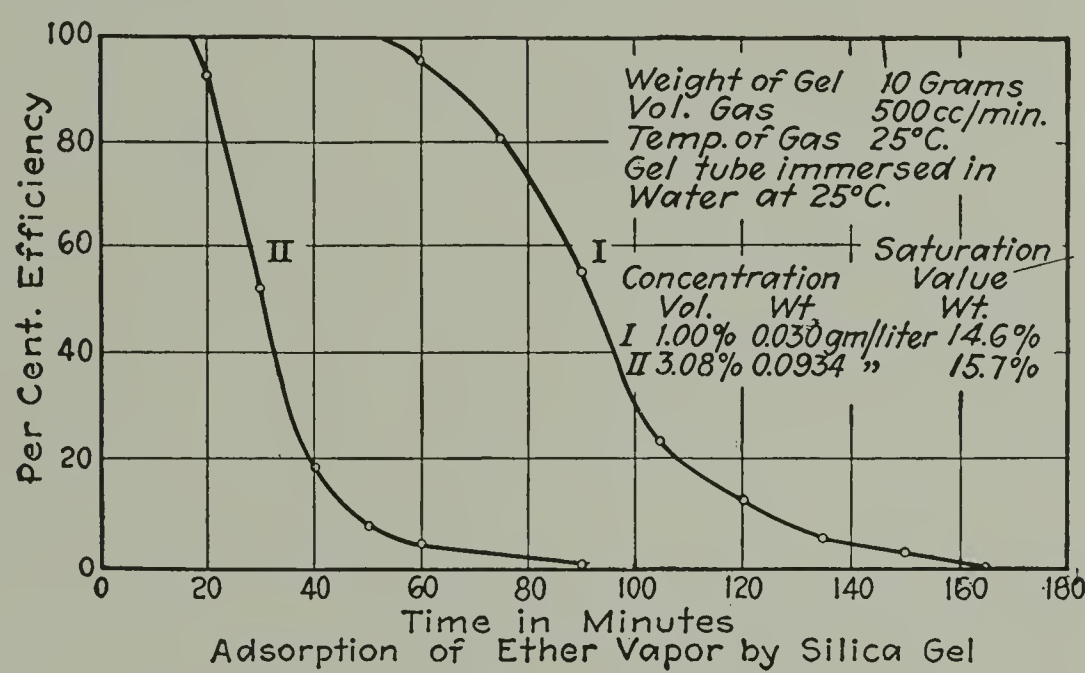

Fig. 6.—Adsorption Efficiency on Ether Vapor.

ing 100 grams of gel with its adsorbed material is connected on one side with a source of steam and on the other with a condenser and receiver, the latter being so constructed that its contents may be drawn off and weighed. When all connections are made the gel is heated to about 105° C. by immersion in an oil bath. During heating some of the adsorbed material generally distills out. When the desired temperature is reached steam is admitted to the gel and the mixed vapors are condensed and collected in the receiver.

In reference to the percentage recoveries of the various solvents as shown in the following pages, it should be pointed out that, working on such a small scale, the experimental errors are relatively large. No very special effort was made to eliminate losses in handling and weighing the distillates.

Ethyl Ether

Adsorption. Figure 6 gives the results of two typical experiments on the adsorption of ether vapor at 25° C.

The desired mixture of ether vapor and air is obtained by saturating a metered volume of air by bubbling it successively through several bottles of pure ether kept at a constant temperature. The resulting mixture may, if desired be diluted by further admixture with air. The weight of ether carried by the air is determined by absorbing it completely from a known volume in a weighed portion of silica gel and noting the increase in weight. From the weight of ether in a known volume, the volume per cent is calculated on the assumption that the gas laws hold for ether vapor, which is of course only approximately correct.

An examination of the curves shows that, using a 1.017 per cent mixture of ether vapor and air, the gel adsorbs at 25° C. an amount of ether corresponding to 14.4 per cent of its own weight; and, using a 3.066 per cent mixture, it takes up 15.5 per cent of its own weight. In each case it adsorbed nearly 8 per cent of its own weight at 100 per cent efficiency.

Recovery. Two experiments were carried out under slightly different conditions.

Experiment 1. 100 grams of gel containing 29 grams of adsorbed ether.
Temperature of condenser 20° C.
Temperature of receiver 0° C.
Receiver vented to air.

	Distillate.		
	Ether.		Water (Grams).
	Grams.	Per Cent of Total.	
During heating to 107° C.	10.209	35.2	None
15 minutes of steaming	14.376	49.5	0.755
20 minutes of steaming	None	None	....
Recovery	24.585	84.7	....

At the end of the experiment, no ether was left in the gel. The 15 per cent loss was due to evaporation through the vent in the receiver and to experimental losses in handling and weighing. We carried out the next experiment using colder water in the condenser in order to minimize the loss by evaporation through the vent in the receiver.

Experiment 2. 100 grams of gel containing 30.5 grams of adsorbed ether.

Temperature of condenser 0° C.

Temperature of receiver 0° C.

Receiver vented through a tube containing silica gel.

	Distillate.		
	Ether.		Water (Grams).
	Grams.	Per Cent of Total.	
During heating to 107° C.	9.769	32.0	....
10 minutes of steaming	17.821	58.4	17.545
20 minutes of steaming	None	None	....
Recovery	27.590	90.4	....

The vent tube absorbed 0.095 gram of ether.

Acetone

Adsorption. Figure 7 shows the results of several experiments on the adsorption of acetone vapor at 25° C. from mixtures with air ranging in concentration between 1.18 per cent to 8.9 per cent acetone vapor by volume.

The mixtures with air and analyses of same were made in a manner similar to that already described for ether. The data given on the curve sheet are self explanatory.

Recovery. We give here the results of three experiments in the recovery of adsorbed acetone.

Experiment 1. A tube containing 100 grams of gel with 33.8 grams of adsorbed acetone was connected with a source of steam, a condenser and a receiver as already described. During the heating some acetone was distilled out and condensed in the receiver but the amount was not determined separately. When the temperature reached 105° C., steam preheated to 112° C. was passed through the gel for a period of 80 minutes. 94.44 c.c. of condensate were obtained which had a density of 0.94094. This corresponds to 33.77 grams of acetone or 100 per cent recovery.

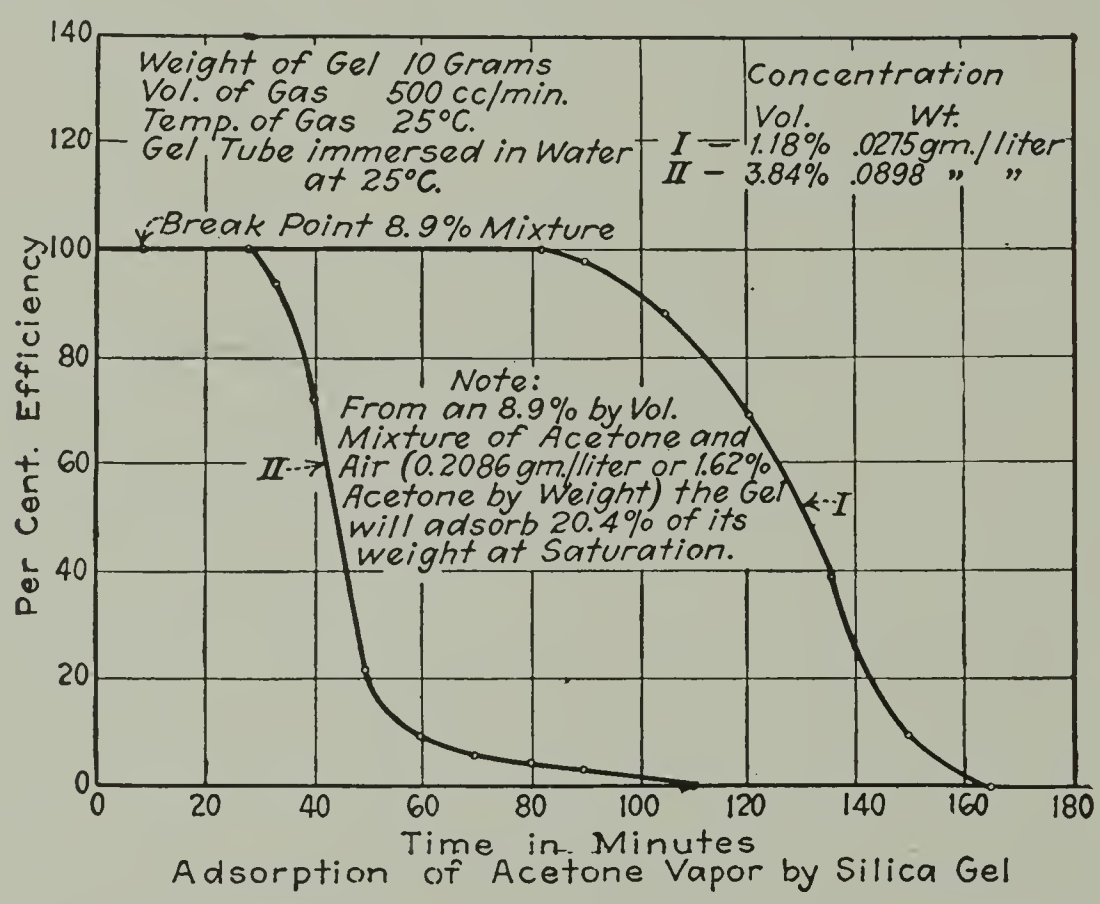

FIG. 7.—Adsorption Efficiency on Acetone Vapor.

Experiment 2. 100 grams of gel containing 33.3 grams of adsorbed acetone.

Temperature of condenser 20° C.

Temperature of receiver 0° C.

Receiver vented to air.

During heating to 107° C. 8.0485 grams of acetone distilled over. Steam was then passed for 20 minutes, giving a distillate of 16.9726 grams, having a density of 0.81529 at 25° C. This corresponds to 15.36 grams of acetone and 1.6126 grams of water.

Further steaming for 30 minutes gave a distillate of 26.69 grams, having a density of 0.9770 at 25° C. This corresponds to 3.87 grams of acetone and 22.82 grams of water.

Acetone recovered from 27.28 grams or 82 per cent of the total.

Experiment 3. 100 grams of gel containing 33 grams of adsorbed acetone.

Temperature of condenser 0° C.

Temperature of receiver 0° C.

6.062 grams of acetone distilled over during heating to 107° C. Steaming for 10 minutes gave a distillate of 34.47 grams having a density of 0.8654 at 25° C. This corresponds to 24.8184 grams of acetone and 9.6516 grams of water. Further steaming gave no liquid acetone.

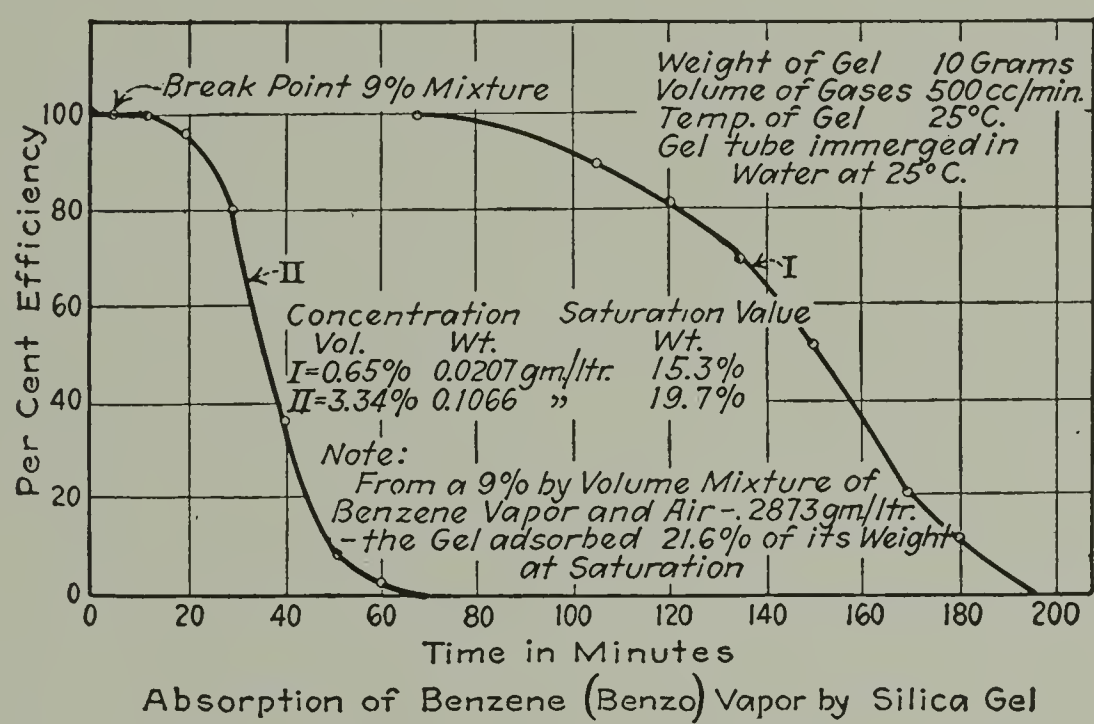

Fig. 8.—Absorption Efficiency on Benzene Vapor

Acetone recovered, 30.8827 grams or 93.5 per cent of the total. During distillation the receiver was vented through a column of gel. Only a negligible increase in weight occurred.

Benzene (Benzol)

Adsorption. Figure 8 gives the results of some adsorption experiments on benzene. The curves follow very closely the corresponding curves for acetone. Concentrations were determined in the manner already described.

Recovery. Two experiments are given, differing with respect to the temperature of the condenser and the amounts of adsorbed benzene present.

Experiment 1. 100 grams of gel containing 21 grams of benzene.
Temperature of condenser 20° C.
Temperature of receiver 0° C.
Receiver vented to air.

	Distillate.		
	Benzene.		Water (Grams).
	Grams.	Per Cent of Total.	
During heating to 107° C.	None	....	None
20 minutes of steaming	17.6282	83.9	4.1755
45 minutes of steaming	0.5489	2.6	51.5
Recovery	18.177	86.5	....

Experiment 2. 100 grams of gel containing 33.5 grams of adsorbed benzene.
Temperature of condenser 0° C.
Temperature of receiver 0° C.
Receiver vented through gel.

	Distillate.		
	Benzene.		Water (Grams).
	Grams.	Per Cent of Total.	
During heating to 107° C.	None	....	None
10 minutes of steaming	30.9716	92.1	6.2852
30 minutes of steaming	1.1515	3.4	54.335
Recovery	32.123	95.5	....

Water

Adsorption. We have seen that silica gel, even after activation, always contains some water. The water content varies between 5 and 7 per cent by weight, depending upon the temperature and time of activation. By prolonged heating in an air stream, the water content may be reduced below 5 per cent, but gel with 5 to 7 per cent gives better adsorption. For the sake of clearness in presentation, we distinguish between this residual water, always present, and adsorbed water.

Figure 9 shows the adsorption of water at 30° C. from air saturated at 30° C., using gel with an initial water content of 7

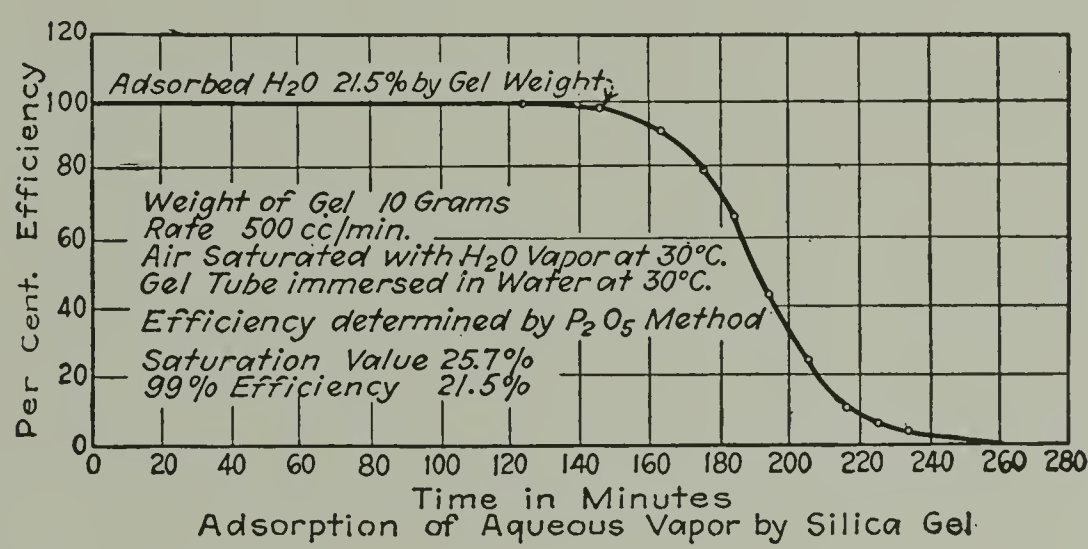

Fig. 9.—Adsorption Efficiency on Water Vapor.

per cent. The air was passed through the gel at the rate of 50 c.c. per minute per gram of gel, thence over weighed phosphorus pentoxide. The increase in weight of the latter gave the water content of the air dried by the gel. For the first two hours the amount of water in the air as it left the gel tube remained constant at 0.3 milligram per liter, which corresponded to 99 per cent efficiency. In other words, the relative humidity of the air dried by gel was 1 per cent. At the end of 2½ hours the efficiency was still 98 per cent and the gel had adsorbed 21 per cent of its own weight of water. Adsorption continued till the gel had taken up an amount of water corresponding to 25.7 per cent of its own weight, which is here called the saturation value.

Figures 9-a, 9-b, 9-c show the drying power of silica gel at 30° C. using air with varying amounts of moisture ranging from 100 per cent to 26.7 per cent relative humidity at 30° C.

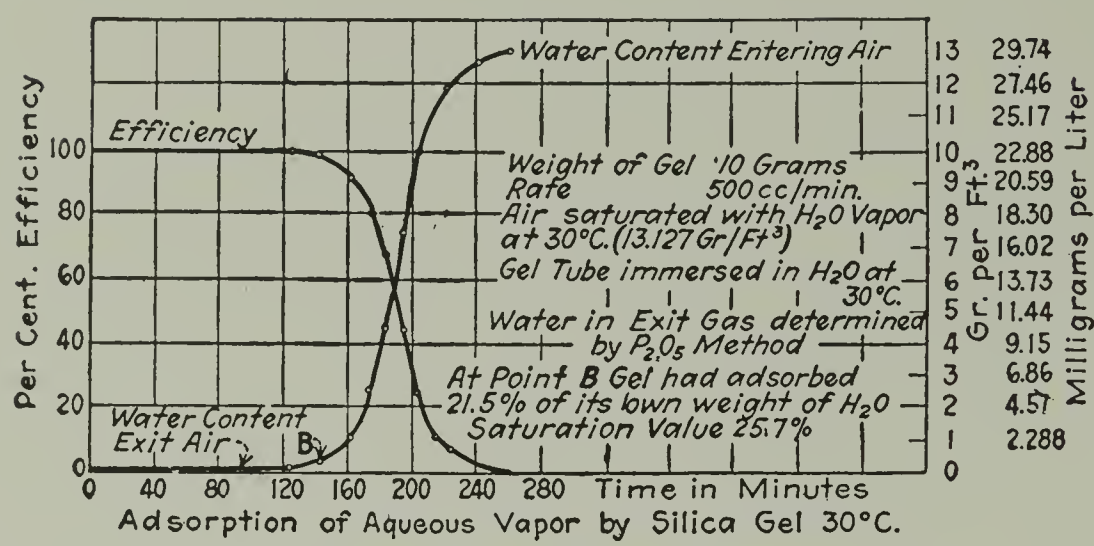

FIG. 9a.—Drying Power of Silicon Gel $P/Po = 1$.

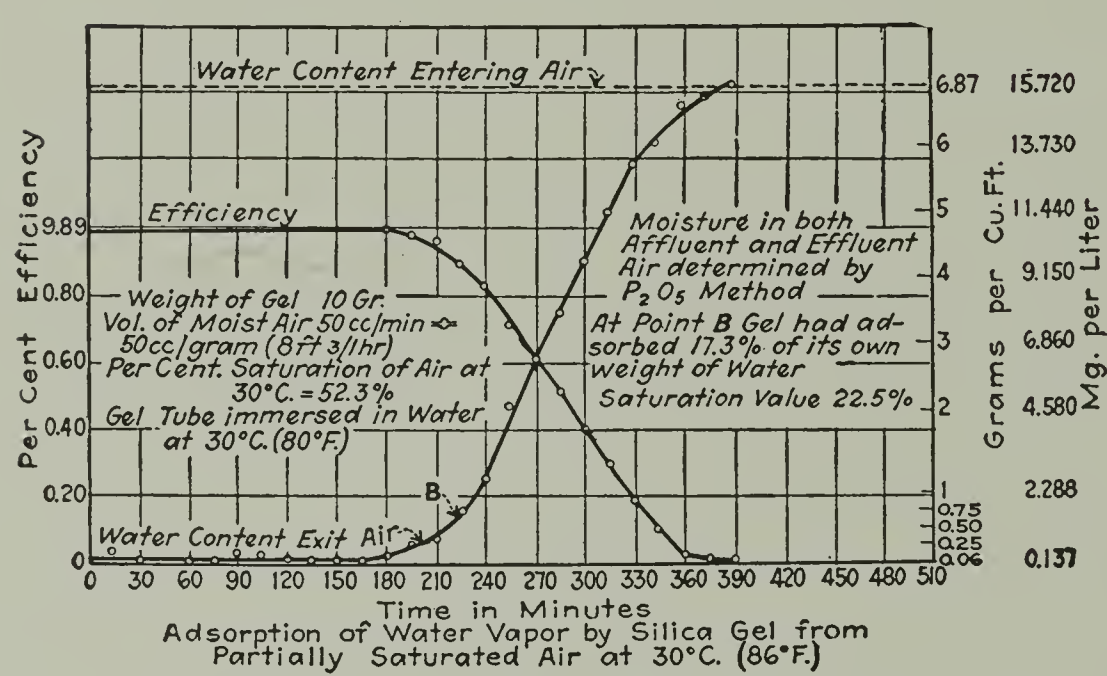

FIG. 9b.—Drying Power of Silica Gel $P/Po = 0.53$.

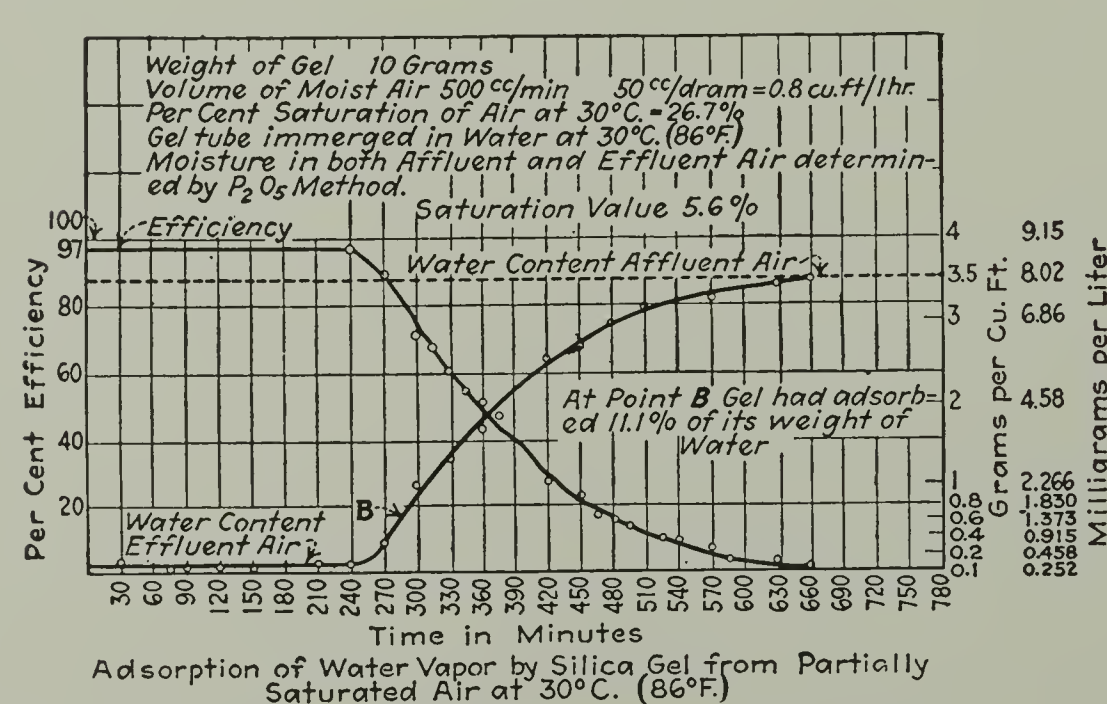

FIG. 9c.—Drying Power of Silica Gel $P/Po = 0.267$.

Figure 10 shows the adsorption of water at 20° C. from air saturated at 20° C. using a rate of 100 c.c. per minute per gram of gel. Here again we have 99 per cent efficiency for 105 minutes, at which point the gel had taken up 18.5 per cent of its own weight of water. Saturation value was 28 per cent.

Removal. Figure 11 gives in graphic form a summary of a large number of experiments on the removal of adsorbed water by air displacement. Experiments have shown that at temperatures from 125° to 200° C., the rate of removal is dependent mainly on the volume of air used, and increases only slightly with increase in temperature. We accordingly do not include here work done above 125° C.

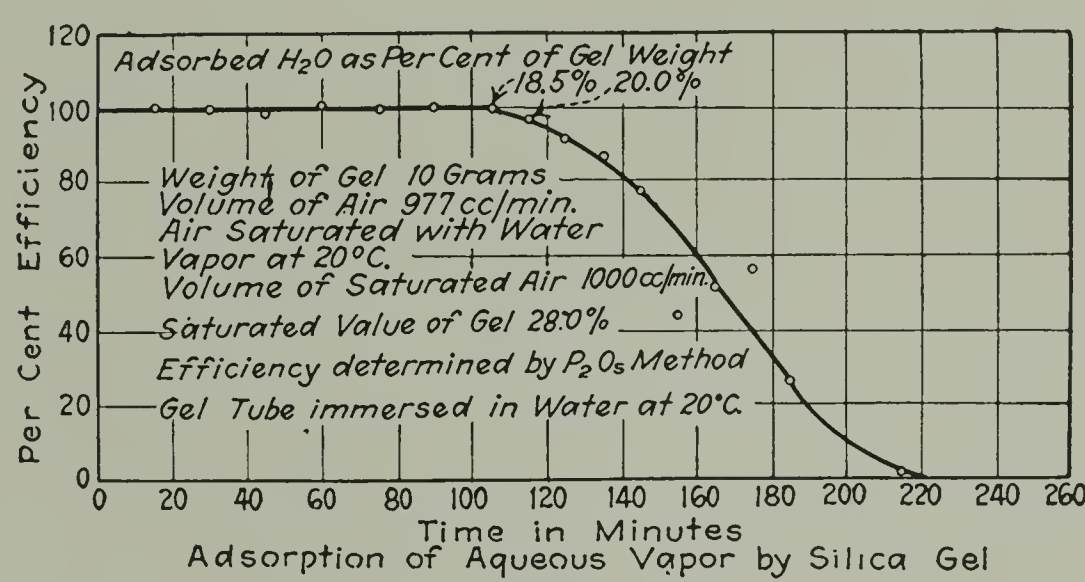

FIG. 10.—Adsorption Efficiency of Water Vapor.

Curves I, II, III and IV show the percentages of adsorbed water removed against time for rates of air flow ranging from 5 c.c. to 50 c.c. of air per minute per gram of gel. An examination of curves III and IV indicates that the adsorbed water is removed about as rapidly with air at 30 c.c. per minute as with 50 c.c. per minute.

Curves V and VI show the same experimental results in which the rate of air flow is plotted against the time necessary to remove 95 per cent of the adsorbed water at 125° C. and 105° C. respectively. An inspection of these two curves will make clear that at these temperatures little will be gained by increasing the rate much above 20 or 30 c.c. per minute per gram of gel.

Gasoline

Adsorption. The results of two laboratory experiments at 25° C. are given in Figure 12. The mixtures of air and gasoline were made in the usual way. The decrease in concentration of gasoline vapor during each experiment was, of course, due to the re-

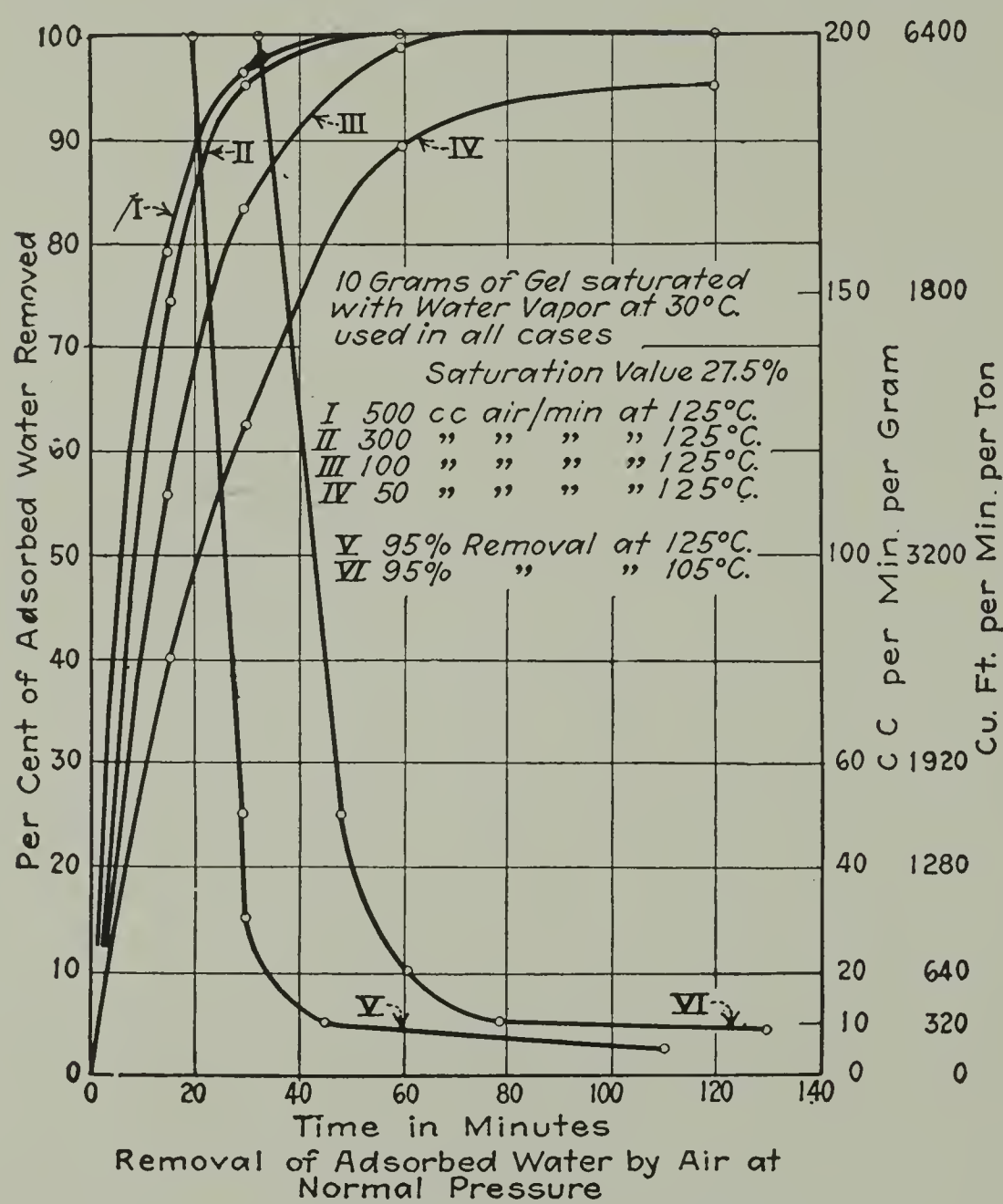

Fig. 11.—Removal of Water from Silica Gel.

moval of the more volatile constituents from the gasoline used to saturate the air.

Recovery. In order to make the tests on recovery of gasoline as rigorous as possible we used in the experiments here described, not ordinary gasoline, but petroleum ether which contains only the lower boiling constituents of gasoline. The hydrocarbon vapors were introduced into the gel in the usual way, viz., by bubbling air repeatedly through petroleum ether at 23° C. to 25° C. and leading

the air thus saturated over the gel kept at the same temperature. For recovery the same procedure was followed as has already been described for other solvents.

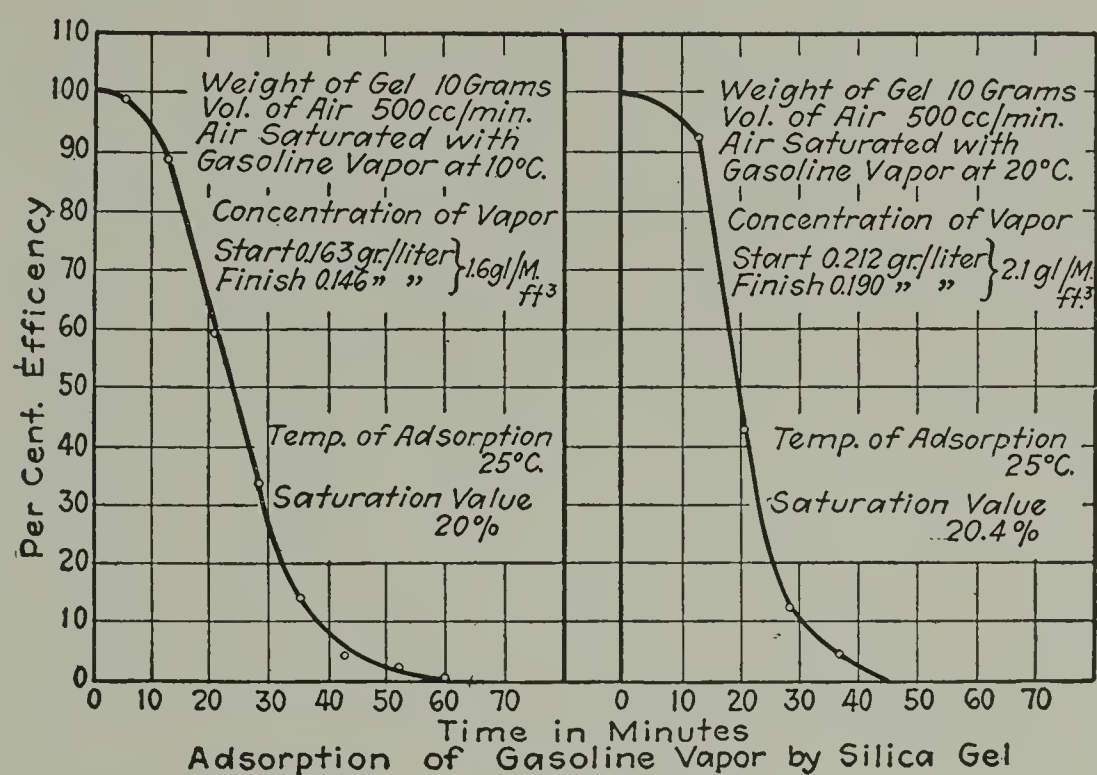

FIG. 12.—Adsorption Efficiency of Gasoline.

Experiment 1. 100 grams of gel containing 15 grams of adsorbed material.
Temperature of condenser 20° C.
Temperature of receiver 0° C.
Receiver vented to the air.

	Distillate.		
	Petroleum Ether.		Water (Grams).
	Grams.	Per Cent of Total.	
During heating to 107° C.	1.1387	7.5	None
10 minutes of steaming	11.1815	74.5	3.6555
20 minutes of steaming	0.401	2.7	11.2215
Recovery	12.721	84.7	....

Experiment 2. 100 grams of gel containing 24.7 grams adsorbed material.
Temperature of condenser 0° C.
Temperature of receiver 0° C.
Receiver vented through gel.

	Distillate.		
	Petroleum Ether.		Water (Grams).
	Grams.	Per Cent of Total.	
During heating to 107° C.	5.104	20.6	None
10 minutes of steaming	18.2625	73.9	11.329
20 minutes of steaming	None	....	....
Recovery	23.3665	94.5	....

The vent tube adsorbed 0.1018 gram of petroleum ether during distillation.

PHYSICAL PROPERTIES AFFECTING PLANT DESIGN

Silica Gel is prepared under carefully standardized conditions and when dried and activated has a moisture content of 5 to 7%. It is a semi-transparent, glassy, brittle, highly porous substance. Its hardness is from 4.5 to 5.5 on the mineral scale and it suffers but slight abrasion with ordinary handling. If, when activated, it comes in contact with water or other liquid, rapid adsorption takes place with evolution of heat and the granules are shattered.

The pores are ultramicroscopic and neither the structure nor adsorptive properties are measurably altered by pulverizing the gel to pass 200 mesh or heating gradually to 650° C. Its internal volume is indicated by the fact that 1 gram of gel will adsorb 0.41 c.c. of water.

Gel sized from 8 to 14 mesh and containing 7% water weighs 44 lbs. per cu. ft.

The resistance of an 8 to 14 mesh gel bed to the passage of air or vapor through it is an important practical factor. Laboratory and

plant results are given in Fig. 13. Plant absorbers have staggered heating flues in the bed which modify the laboratory test conditions.

During adsorption the heat of condensation is liberated and, despite radiation losses, a rise of as much as 25° C. in gel temperature has been noted when there was no attempt to cool the gel by ventilation or water jacketing during the adsorption cycle.

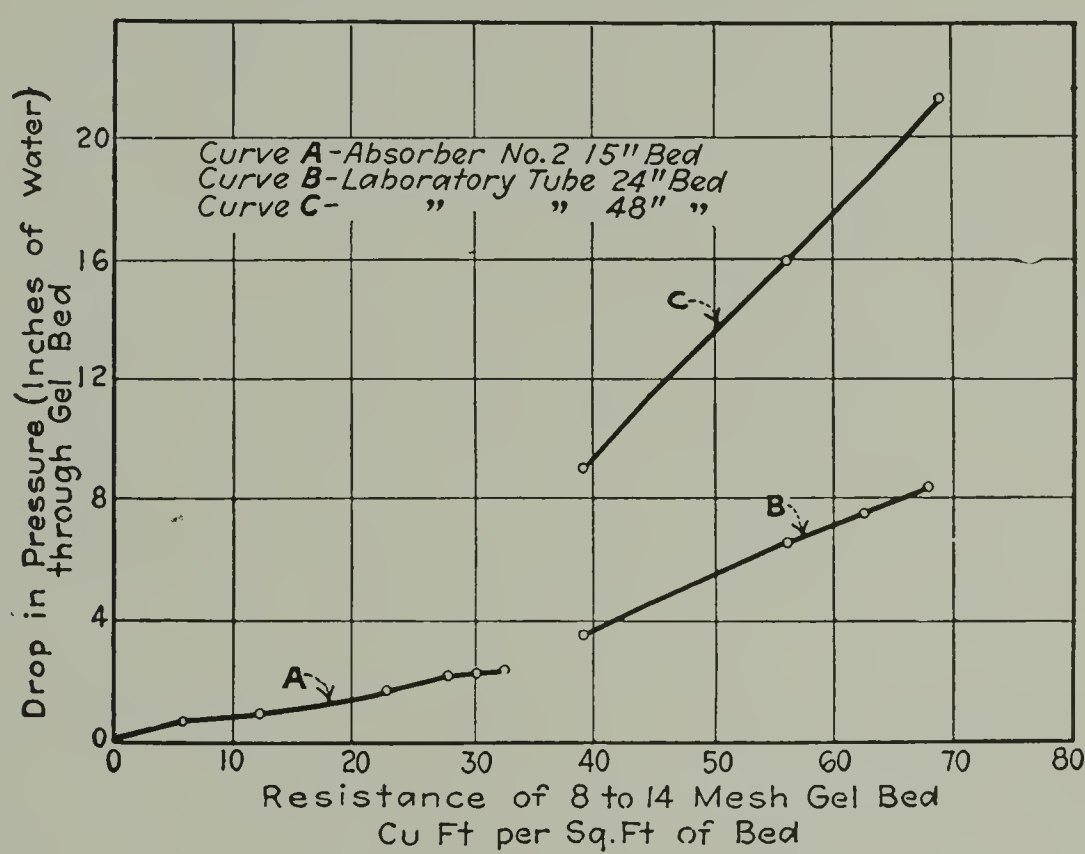

FIG. 13.—Resistance to Vapor and Gas Flow.

Gel can be used either in the granular or pulverized form and the work with semi-commercial scale bed type absorbers for granular gel, and that now under way with pulverized gel will now be described.

BED TYPE ABSORBERS

The first plant absorber is shown in Fig. 14. It is a vertical cylinder with vertical heating and cooling tubes 1″ diameter on 2″ centers passing through the gel bed which is 26″ deep supported on a screen about the middle of the cylinder. Hot gases or cooling air or water may be passed vertically through the tubes and the gas for adsorption enters and leaves by side outlets below and above the gel bed, which contains 250 lbs. of 8 to 14 mesh gel. Most of the practical work on SO_2 adsorption and recovery was done with this absorber.

The first absorber did not have welded tubes, and to overcome difficulties in keeping it tight and getting even distribution of the heat, the second absorber was built.

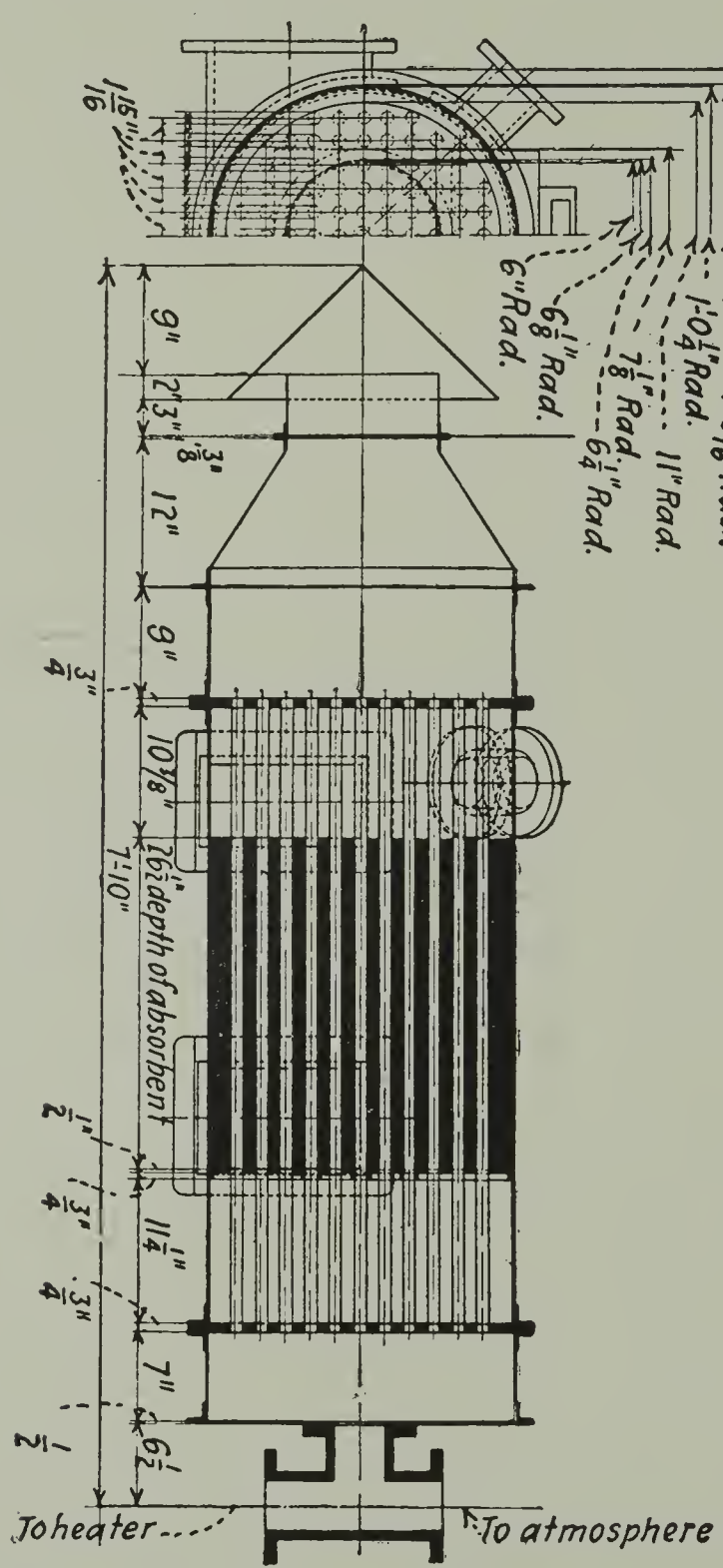

FIG. 14.—Vertical Cylindrical Absorber.

Figs. 15 to 18 show the second bed type absorber plant. The absorber *A* is a rectangular steel box 3′9″×3′6″×2′10″ high with a 420 lb. gel bed 9.75 sq. ft. by 13″ deep supported on a perforated metal screen. Through the gel bed passes a series of horizontal 1″ tubes on 2″ centers. These tubes are welded to the tube sheets which

are enclosed on both sides of the absorber by flue boxes so that combustion gases, air or cold water can be run through the tubes to heat or cool the gel.

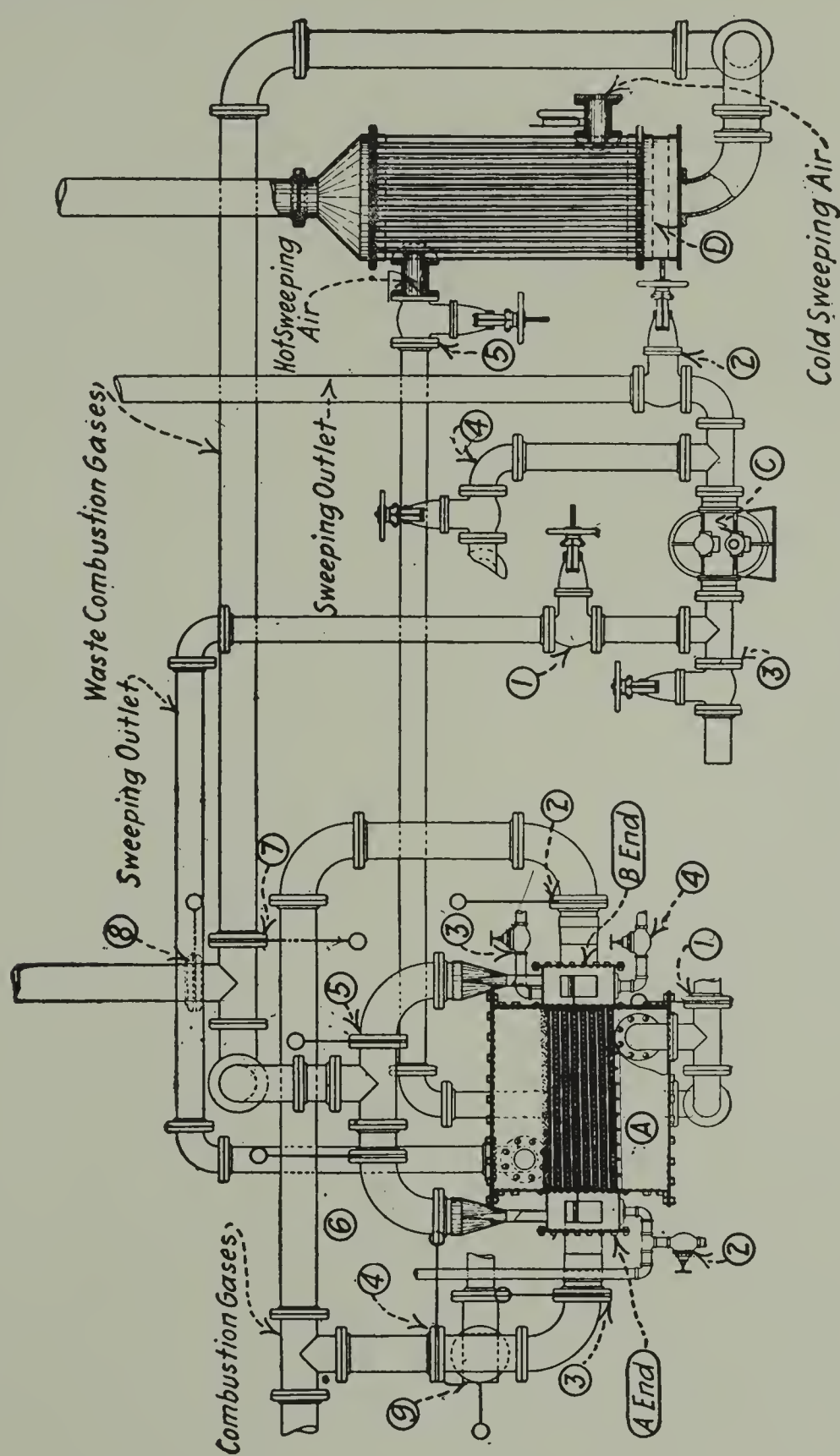

FIG. 15.—Bed Type Absorber Plant.

The plant as shown is arranged for drying air. The air enters through an orifice meter *B*, Figs. 15 and 17, passes into the absorber *A* at the lower right corner and up through the cool gel bed where it is deprived of its moisture, thence by the upper left corner of the ab-

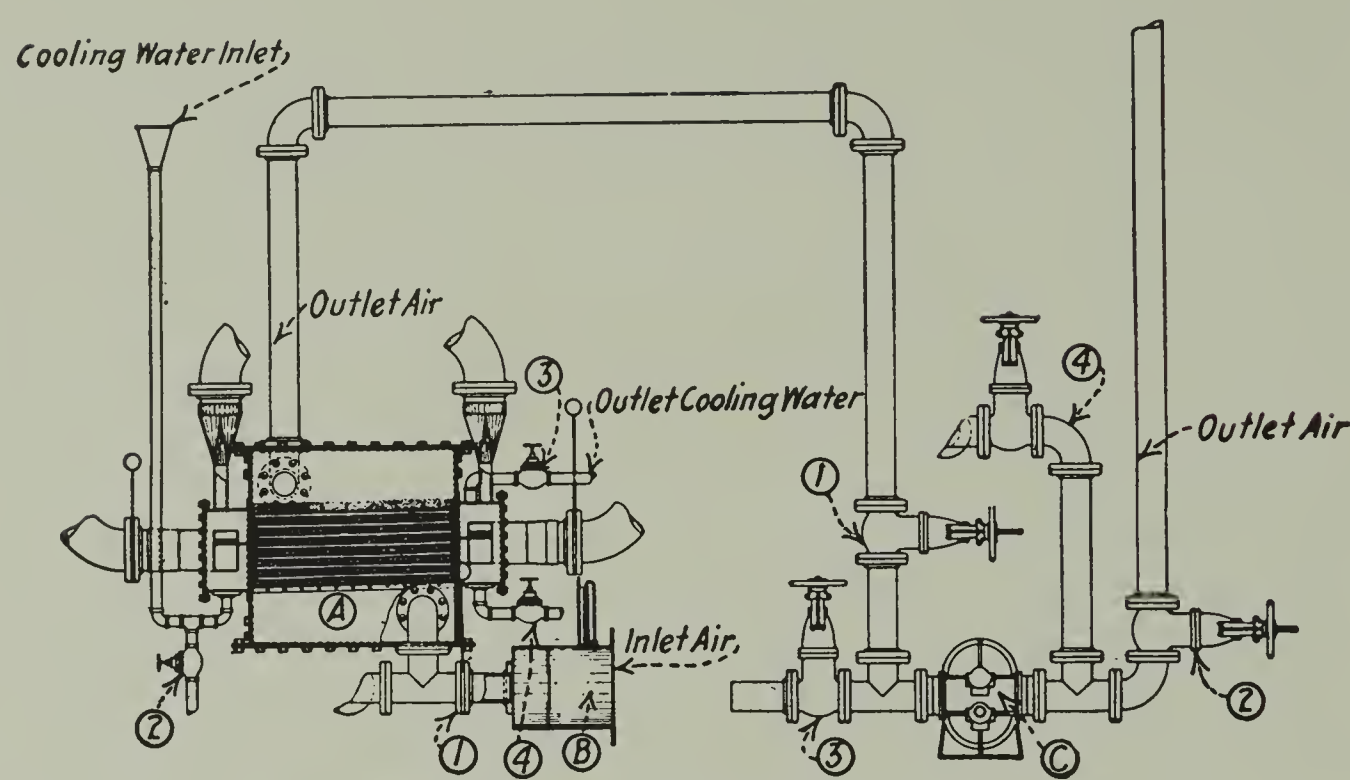

FIG. 16.—Adsorption Cycle.

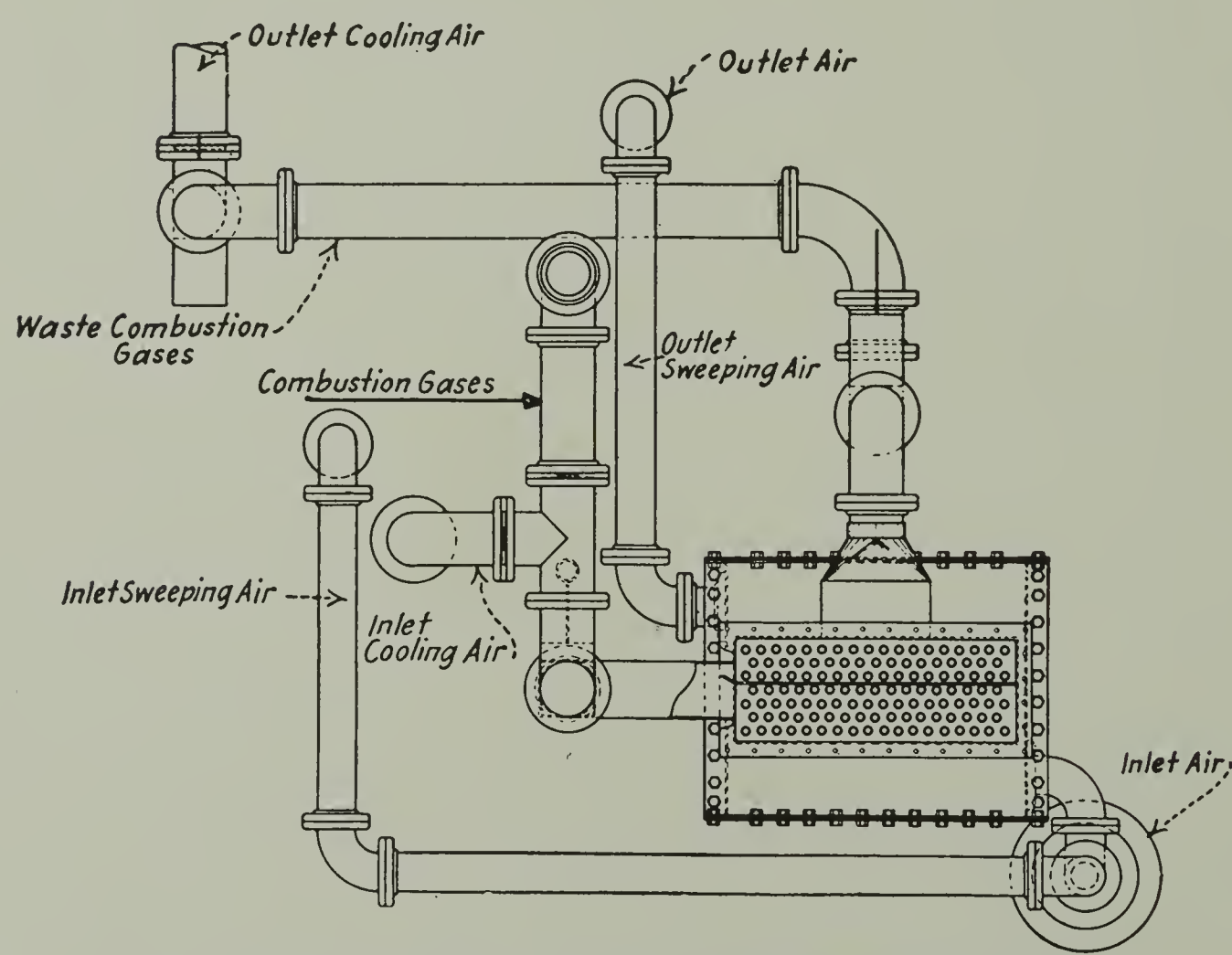

FIG. 17.—Front Elevation of Absorber with Flue-box Cover Removed.

sorber through valve No. 1 to a Roots exhauster *C* and out by valve No. 2 for use as desired.

If it is desired to continuously make a high extraction of the vapor,

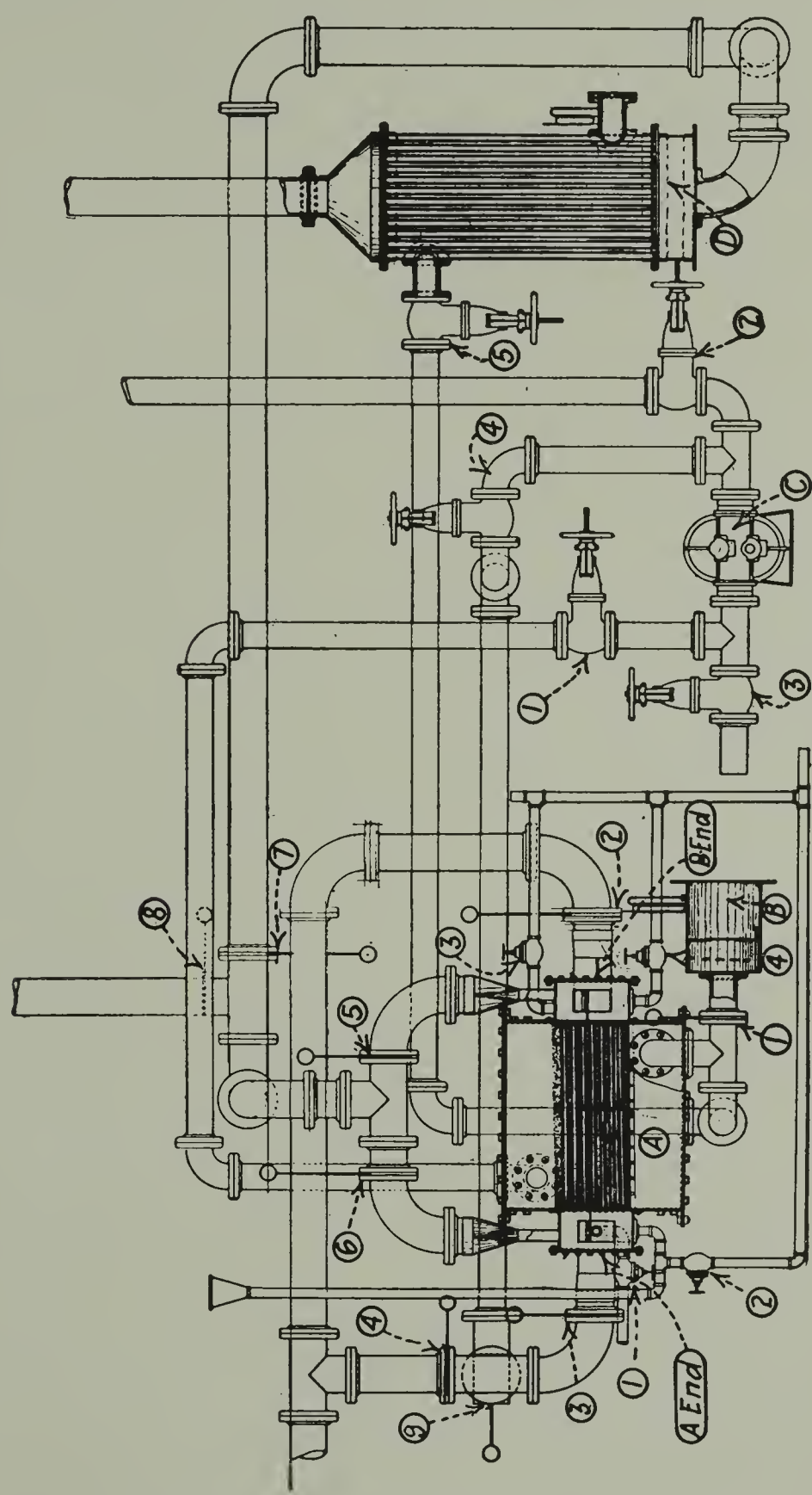

Fig. 18.—Heating Cycle.

a second absorber should be connected in series when the effluent from absorber *A* indicates it is reaching the break-point and absorber *A* is continued in circuit until the gel is saturated. The air is then

cut off at damper No. 1 and the gel is dried or reactivated by heating and sweeping hot air through it. The heating or evacuating cycle is shown in Fig. 18. Combustion gas or hot blast is admitted alternately by the dampers Nos. 2 and 3 passing through the tubes in the gel and out by dampers Nos. 5 and 6 to the heat exchanger *D*. Air is admitted to the heat exchanger on the lower right side, is heated and passes through valve No. 5 to the bottom inlet of the absorber thence through the gel to the blower and to waste through the valve No. 2 carrying with it the released moisture.

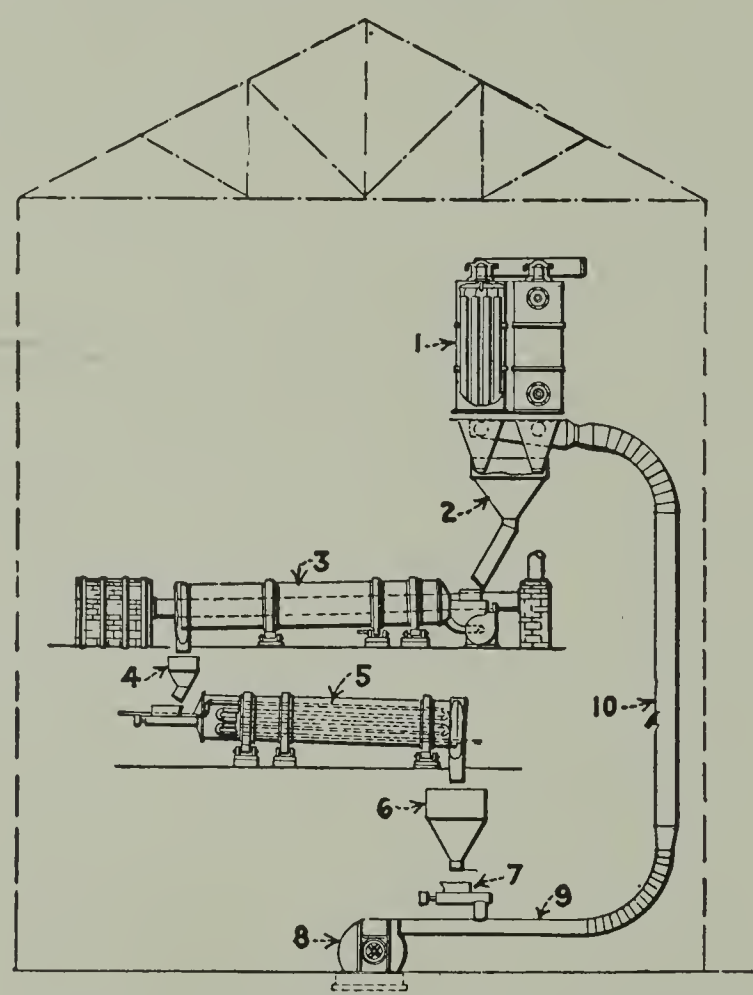

FIG. 18A.—Flow Diagram Pulverized Gel Plant.

When the gel is dried cooling may be hastened, if necessary, to prepare it for the next absorption cycle, by blowing cold air from inlet valve No. 3 through valve No. 4 and dampers Nos. 9 and 3 through the absorber tubes and out by damper No. 5. Water spray is use with this cooling air at the start and the tubes and flue boxes are flooded with water when the emperature is below the boiling point. The next cycle can be started when the temperature has been reduced to 75° C. as the air being dried will assist in the cooling and the jacketing water will lower the gel to a moderate temperature before the break-point is reached.

The air drying tests were made in this absorber.

A third type of bed absorber using granular or unsized gel flowing slowly through a louvered or screened compartment thus making a continuous absorber is under consideration

PULVERIZED GEL ABSORBERS

For continuous operation and uniform product three fixed bed type absorbers are needed so that a second one can be put in circuit a safe interval before the first one reaches its break-point while the third one is on its heating and cooling cycle.

In the pulverized gel absorber the activated dust is fed into the gas stream discharging into a dust filter, adsorption taking place in the duct and filter bags.

This method is attractive from several points of view.

First. It requires only standard equipment such as is regularly used in feeding powdered coal and in dust separating in metallurgical plants.

Second. It seems clear that a smaller quantity of gel would be required for a given duty than with a bed type absorber, because there is no time lost in heating and cooling an absorber nor is there any idle gel in an absorber bed.

Third. The heat is economically applied since the heater is always hot, as against the intermittent heating and cooling of the bed absorber.

Preliminary tests in the laboratory using 80 and 200 mesh gel in a current of air with 2 to 6 grains of moisture per cu. ft. reduced the effluent in one stage to from 1.0 to 1.3 gr. In the above tests the time of contact between air and gel did not exceed 4 seconds, which later experiments have shown to be inadequate. Apparatus now under construction will permit longer and better contact.

EXPERIMENTAL PLANT RESULT

Sulphur Dioxide

Adsorption. A large number of tests were made with the No. 1 absorber on the adsorption and recovery of sulphur dioxide from air mixtures ranging in concentration from 2.5% to 8.75% by volume. The data are too bulky to include in this paper.

Fig. 19 gives the results of a typical run on adsorption from an 8.75% mixture. The mean temperature of the gel at the end of the run was about 40° C. and it adsorbed 17 lbs. of sulphur dioxide or 6.8% of its own weight.

Referring to the curves already given it will be seen that this corresponds approximately to the saturation value.

Recovery. A number of tests in the recovery of adsorbed sulphur dioxide were made, using absorber No. 1.

Starting with an 8% mixture of sulphur dioxide and air, the gel adsorbed 5% to 6% of its weight of sulphur dioxide. The absorber

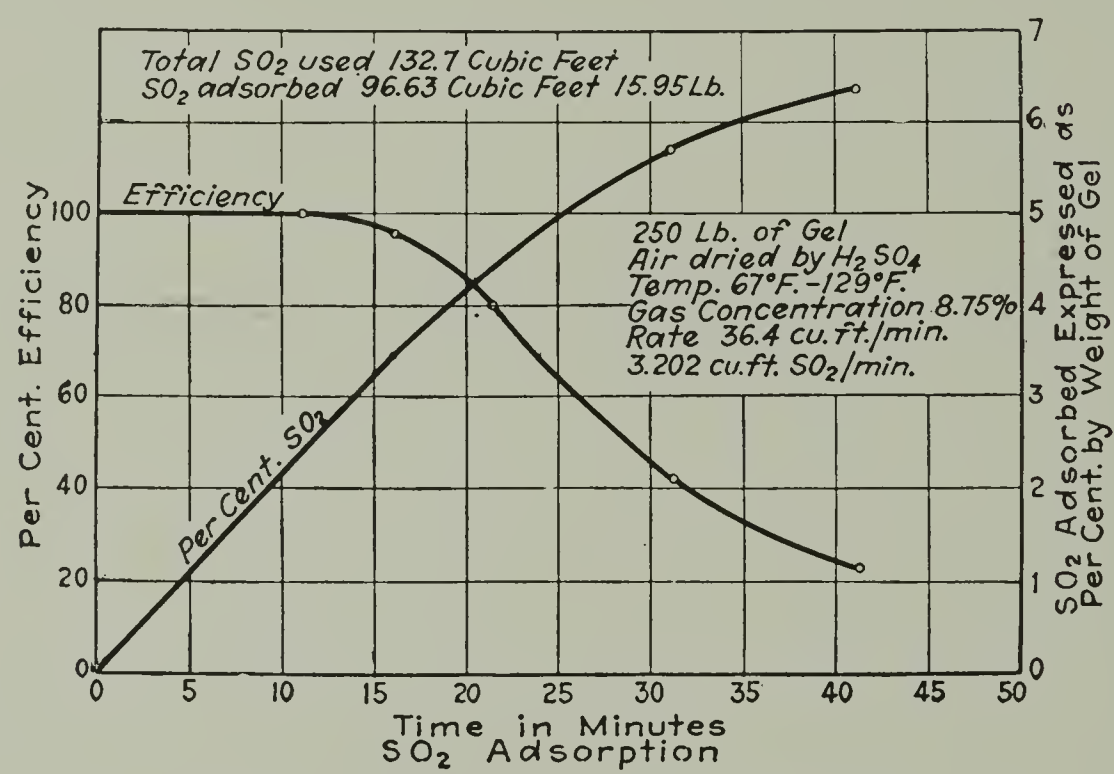

FIG. 19.—Plant Record on SO_2 Absorption.

was then heated to about 125° C. and the gas pumped off. Most of it came off at a 25-inch vacuum. The liberated gas was liquefied at 25° C. by compression. The details of these experiments need not be given here.

In other tests, the gas was delivered by the vacuum pump directly to a dry gas meter. At frequent intervals, analyses of the gas were made and the volume noted.

Fig. 20 shows the results of a typical run made in this way. It will be observed that the absorber was partially evacuated for a few seconds before heat was applied and the gas wasted for this brief interval, in order to eliminate as much of the air in the apparatus as possible without waste of sulphur dioxide. The first analysis made at the end of four minutes when the temperature of the gel was about

65° C., showed 85% sulphur dioxide. In plotting the curve which expresses the gas liberated as percentage of the total quantity adsorbed, it was assumed that the average composition of the gas during the first 4 minutes was 57%.

Making this assumption we see that during the first 18 minutes, about 90% of the total gas was liberated at a mean concentration of 75%. The 25% air resulted partly from the air originally present in

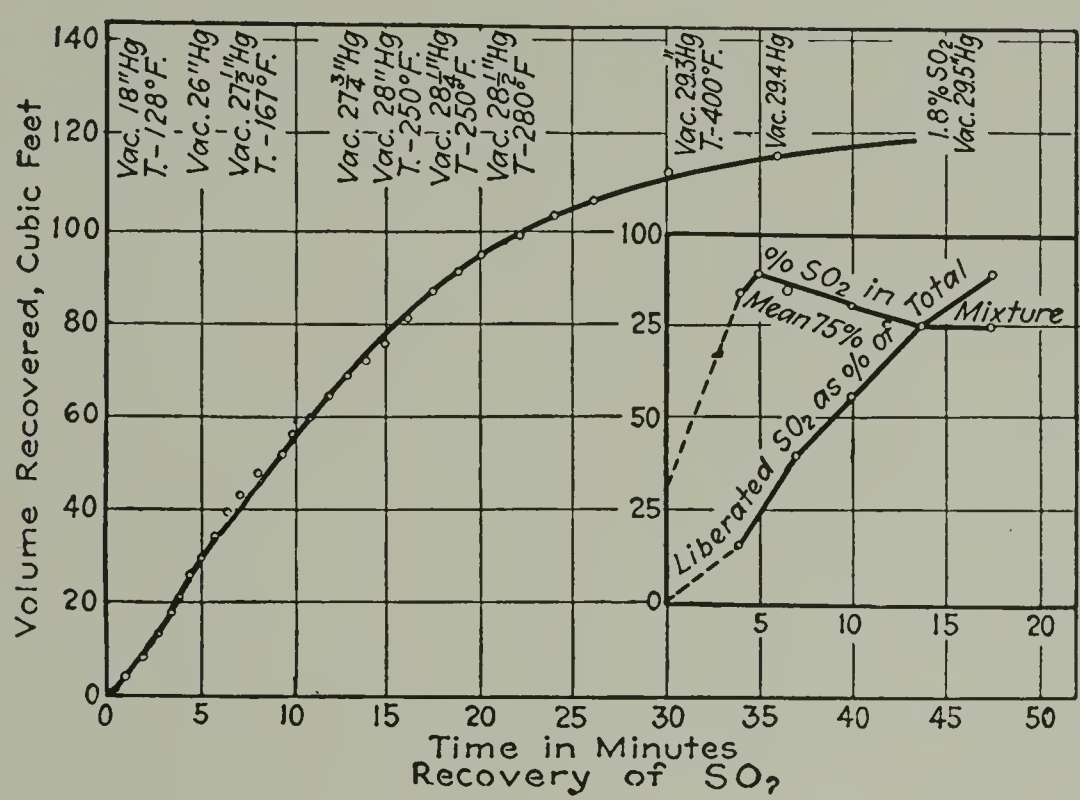

FIG. 20.—Typical Plant Record.

the absorber and connecting pipes, but mainly from leaks in absorber, valves and pump.

AIR DRYING

Fig. 21 is a composite of the results obtained in eight runs with the second absorber with an air current through the absorber of 330 cu. ft. per minute or at the rate of 33.8 cu. ft. per square foot of gel bed or 0.78 cu. ft. per lb. of gel. These runs were made in March so that unfortunately the atmospheric humidity in none of these tests exceeded 5.3 grains per cu. ft. Few of our large scale tests as yet show the sharp break-point obtained in the laboratory work, but it will be noted that if we assume the allowable end point to be when the dried air rose in water content to 0.7 gr. per cu. ft. the gel was in service an average of 3 hours, or that one 420 lb. absorber dried over

59,000 cu. ft. of gas before the water content of the outgoing air rose to 0.7 gr.

The 0.7 gr. end point is assumed because it is below the moisture

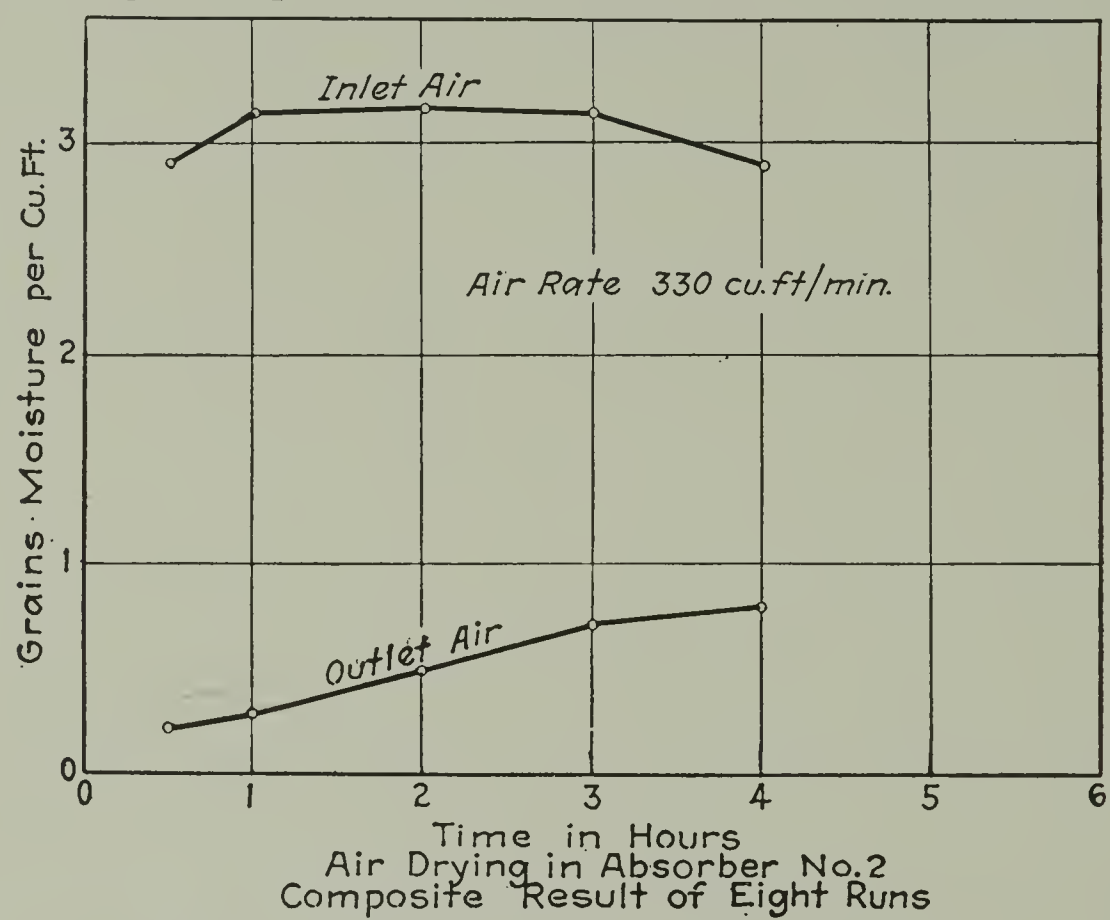

FIG. 21.—Composite of Eight Runs on Drying Air.

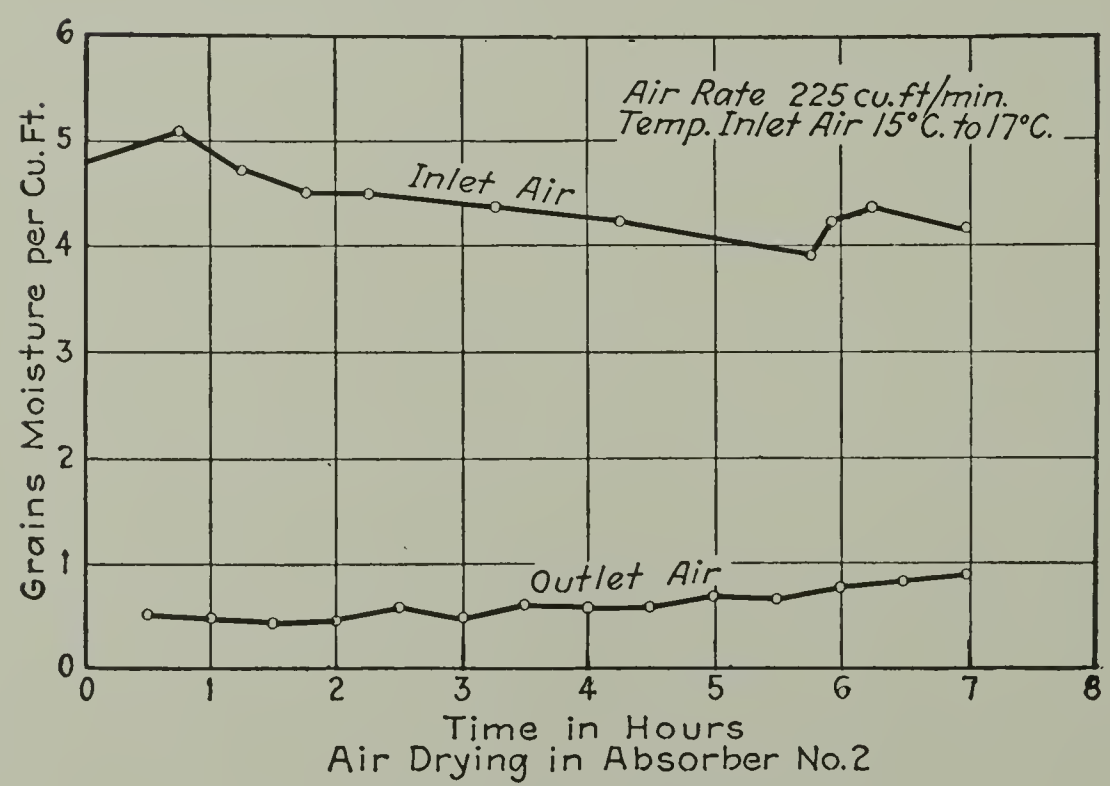

FIG. 22.—Drying Air at the Rate of 225 Cu. Ft.

content in any continuous run of a Gayley dry blast plant of which we have record.

Fig. 22 is of a run at 225 cu. ft. per minute rate when the humidity

averaged about 4.5 grains per cu. ft. and the outlet air reached the 0.7 gr. end point in 4 hours, 45 minutes, finally rising above this point in $5\frac{1}{2}$ hours. When atmospheric humidity was below 2 grains runs of six and seven hours have been made without reaching the 0.7 gr. end point.

INDUSTRIAL APPLICATIONS

It will have been seen from the preceding discussion that silica gel is adapted to recovering practically all volatile liquids. This property may be applied to the following amongst many other practical commercial problems:

Drying Air	Air conditioning
	Dry air blast for furnaces
Gasoline recovery	From gas wells
	Casing head gases
	Losses from storage tanks
	Losses in oil refineries
Solvent recovery	All industries using volatile solvents
Recovering industrial gases	Notably sulphur dioxide and oxides of nitrogen
Selective separation of mixed gases.	

A more specific list of possible applications is not within the limits of the present paper. While much remains to be done to reduce the above applications to practice, we feel that the theoretical and scientific aspects of the problem have in the main been solved, and that there are no insuperable mechanical difficulties to be overcome.

Acknowledgments

The work necessary for the preparation of this paper was divided into three general groups, and entrusted to members of our Research and Engineering Staff as follows:

Theory.....Dr. Walter A. Patrick
Laboratory Results.....Dr. B. F. Lovelace
Experimental Plant.....Mr. E. C. Holden

THE MANN REPORT ON ENGINEERING EDUCATION

Read at the Montreal Meeting, June 28, 1920

By A. W. SMITH

Some years ago the teachers in our American institutions for higher education were thrilled by the announcement of a wonderful gift, that of Mr. Carnegie, for the advancement of teaching. This consisted in a large endowment fund for the purpose of granting pensions to retiring professors so that during their productive years, they might be free from the worry of providing for old age. Mr. Carnegie's thought was that this would attract competent recruits to the college faculties as well as conserve those already enlisted, from the attraction of higher money rewards available in most other lines of endeavor.

The plan started most auspiciously under the direction of a board chosen from a wide range of institutions. This board began on the sound plan of assisting only the teachers in institutions that were doing an educational service worth while, at the same time assuming that state and denominational institutions should of right, care for pensions for their own retiring teachers, if any were to be given them.

This led naturally and properly, to the necessity for determining what institutions were doing worth while work and of setting up standards, by which the various institutions could be classified and judged.

This again made the government board of the Carnegie fund to a degree, an arbiter of the quality of American institutions for higher education and gave it a sort of autocratic power over them which on the whole has been used with great wisdom and excellent results. In order that the board might use this power with proper knowledge of all the conditions surrounding our educational institutions, they have made various studies of these institutions and have published reports giving the results of such studies, one of which

is that under consideration. This one did not stop with reporting the conditions and facts learned, but proceeded to criticise freely and to recommend liberally. Unfortunately the author was neither a practicing engineer, nor had he any wide personal experience in engineering education before entering upon the preparation of this report. It is true that the report as a whole was approved by a committee of Engineers, but it would be a matter of much interest to learn to just what extent this committee associated with the report, proposed or controlled its criticisms and recommendations.

The result is to my mind, pretty much what would be expected if one of us were asked to make a report on the theological seminaries or law schools of the country, and we should spend sufficient time to visit the important centers of such education, talk with their boards of control and their faculties, and correspond with many of their graduates. Among the last we would hear most from the superficial and the disgruntled and among the faculty members we would undoubtedly be most impressed by the extremists and the faddists, because they would be the most voluble and eminently the most enthusiastic. Our recommendations would naturally be a composite of such fads and unjudiciously criticised views.

I am led to offer the following criticisms of the report only because of the great eminence of the auspices under which it was made and published and which apparently stand for its recommendations in entirety. This causes it to be looked up to by many as final in its authority and infallible in its wisdom. The result is likely to do harm in a broad sense to engineering education, unless the fads are recognized and put into their proper subordination, and the extremists' views moderated. The present general plan of engineering education, now quite similar in all the best schools, is the result of a process of evolution of many years, under the combined advice of the best engineers and educators the country has produced and is constantly under the scrutiny, questioning and criticism of such experts. Probably no other subject receives so much attention from our engineering societies. It has a similar society all its own, the Society for Promotion of Engineering Education, composed of eminent experts for the sole purpose of improving such education. While of course, not final, the present

methods should not be radically and suddenly changed except for very well considered reasons and then not without experience and moderate experimentation.

What does the report define as the purpose of an engineering course? On page 88 we find "The college curriculum should aim to give a broad and sound training in engineering science, rather than a highly specialized training in some one narrow line." On page 90 we find, "The real purpose for which engineering schools were established is to *increase industrial production,*" which is called the *"fundamental aim of engineering"* to be used in framing a curriculum. Two goals could not be more widely separated. It presents this advantage to the author, however, that if it is pointed out that the results of any particular suggestion take you away from one goal, he can easily prove his point by showing that it will take you toward the other one. The chapter of the report entitled "The Professional Engineer" would even seem to indicate that following the recommendations made would lead to neither of the above goals. In this chapter all technical knowledge and skill are practically eliminated from the qualities essential for the success of the engineer, taking the lowest place in the scale of requirements. This character group of qualities, placed at the head of those desirable for the success of the engineer are no more demanded for the success of the engineer than they are for the success of the individual in any other walk of life, professional or otherwise. To say that a man has all these qualities is not to say that he *will* succeed but that he *has* succeeded. The most important are fundamentally qualities that are born in men, or inoculated into them in the home, beginning at birth and by all the process of schooling prior to the college. Of course the instruction in the engineering school should stimulate and not hinder the development of the student in these respects but the question might be asked, "Is it the province of the engineering schools to take young men of character and train them to be engineers or to devote their time to the training of men for executive positions and productive managers?" If the latter, who will train the engineers?

The author here seems to fall into the common fault of those who expect the engineering school not only to train the undergraduate broadly in the principles of engineering so that he may make a start in its practice, but also to fit him for the work to

which he will properly advance only five or ten years after graduation. The industries and the profession itself have a co-ordinate responsibility with the college for the training and success of the young engineer, which they should not, and generally which they do not want to shirk, when it is clearly recognized. Training for plant management and executive positions, for plant output and plant sense is the province of the industries and the profession broadly, because only here can it be well done. On the other hand, the giving of the "broad and sound training in engineering science" and its fundamentals is the duty of the engineering school to its undergraduates. If this is done well, very little time outside of vacation periods and some college laboratory courses will be left for any other use. If underlying and broad principles are not gained in undergraduate life, they are only rarely acquired later.

Anyone would know as the report points out, that "the opportunity for the college trained engineer is now very much larger in the field of production and administration than in the field of design." The report seems to consider this a discovery and to emphasize the "now," though it has always been true and is here only rediscovered. Each of our graduates discovers it anew as soon as he takes up the duties of his new plant work. Many of them want the general manager's job at the end of the first six months and are impatient because the plant authorities do not consider their college course as exactly a complete training for success in such places. The ordinary college course surely has ample difficulty in fitting its graduates properly for the job awaiting them at graduation. Those with character, executive ability and tact do not have to wait long for the beginning of that promotion that will some day make them leaders.

The report lays great stress, in criticising present methods of instruction, upon the fact that less than 5% of production managers in this country are college trained men, and says this is due to "the lack of the sense of the physical properties of matter," whatever that may mean. Is it not rather because the engineering graduate goes by preference usually into the engineering, or research or development department, and not into the plant or shop? And which field is really of greater importance to final production and the welfare of mankind, that which invents or designs a new, cheaper and better and greater labor saving process and installs

it in successful operation, or the man who drives it to maximum capacity after its installation? It might be more interesting to compare the percent. of college men who started work in the shop and later became managers, with the percent. of men not college trained who started in the shop and had similar promotion. Possibly the above percent. would be reversed.

In preparing a curriculum the recommendation is made that it be in the hands of a faculty committee on instruction, who are to determine what particular industrial work there is in the locality of the school which may be available for student work and then select the "type of co-operative industrial work that seems best suited to the peculiarities of the environment of each particular school." While the practical work used to illustrate the principles and sciences of engineering taught may and should be taken from the field that absorbs the large percentage of the out-put of the school, to formulate the curriculum to give "a broad and sound training in engineering science" and to base it upon "the type of co-operation industrial work available in the particular locality" seem, as an experienced engineer has said, "like turning the educational structure upside down, and which would result, on account of the specialized character of such industry, in leaving out much of the fundamental parts of the broad training desired. In any case, is not the character of the industrial labor that the student can do, of such a simple nature, that the best curriculum that can be built upon it would be more fittingly styled a bungalow than the great educational structure for which we are striving?"

In regard to a committee of the faculty deciding what shall be taught in each department to constitute the course for graduation, should not the responsible head of that department be the most competent to judge not only what subjects should be taught, but the time to be allotted to each? I am sure some of us would not feel exactly competent to settle the curriculum for a course in civil or electrical engineering or to offer much advice regarding it.

Sixteen credit hours are recommended as a proper limit for the curriculum, which is less than most courses require at present, but the statement follows that it is not intended to decrease the work done per week. Of course, this has little meaning. We all know that the amount of work required is what is sufficient to

keep the average student healthily occupied, no matter how the required hours are named.

The recommendation that in general fewer subjects be taught at a time is excellent. The plan of introducing practical engineering work in the freshman instruction is certainly pretentious, but if shop work or its equivalent is meant, this is generally present practice, while surveying is an eminently proper freshman subject because the freshmen already have a knowledge of the mathematics upon which it is based.

It is suggested that more instruction in one specialized branch be given to students specializing in another than is now common. In general such a plan would not be compatible with four years of study, nor with only 16 credit hours. It is certainly desirable to carry this plan to the limit of the time available, because it adds just so much to the breadth of undergraduate training. This is the most common suggestion of those who discuss engineering education from any angle, namely, to *add* something, but in the best schools, the present courses just about fill up the time and ability for work of the average student. I have never yet heard a critic suggest the elimination of anything from an engineering course so that something might be added, except to suggest the dropping of modern language. I wonder how many of our Institute members would agree to this elimination, advocated in the report, until at least one modern language is made an entrance requirement, and still maintain that such a course trained the graduate broadly in chemical engineering.

A curious inconsistency is found on page 25 in reference to the recommendation as to the time at which students should elect their specialty, where objection is made to the general plan of choosing as early as the end of the first year. Yet, in several places the report lauds the curriculum of a particular school where the student elects his specialty before entrance, because he takes up in his freshman year practical work in the line of the branch of engineering he intends to follow. Most of the twenty-nine special courses mentioned on page 25, from which the student is said to be obliged to make selection can all be grouped under the general heads of Civil, Mechanical, Electrical, Mining and Chemical Engineering, requiring an early choice only among these, while the sub-branch

need not generally be selected until the senior year. Most schools follow this plan now.

After completion of the studies common to all, preferably at the end of the second year, the student according to the report will have shown an inclination toward certain lines of work, as indicated by objective tests and the manner in which he has completed the common studies. He would then not choose, but be "claimed by the special field for which he is fitted." It is a matter for question whether this suggestion contemplated the predicament of the brilliant student when each special field represented by the head of the department personifying it, came collectively to claim its own, or of the predicament of the poor, undesired student, not so claimed by any special field.

An excellent suggestion is made that smaller schools confine their attention to the general studies only, or specialize in one or two groups, as is done at Thayer and was done at Renssalaer. Unfortunately, in general, the smaller the school and endowment, the wider the field it tries to cover.

Much is said of the small proportion of those graduated to those entering and present methods both of entrance requirements and of teaching, are largely held responsible. I wonder if the author has ever taken the trouble to investigate the actual causes of such mortality. Those who have know that the greater portion leaves through no fault of the college or its methods, but because of ill health, financial reasons, or lack of desire and purpose to do the work required.

In this connection the most curious recommendation of all is found as follows:

"It may also be best for many students to leave school when they have completed their general work, especially if leaving should be accompanied by a suitable certificate or diploma."

This would indeed eliminate a large share of the mortality, but what kind of a record would such a school soon have when those who had left with only half of a course and with a half diploma in hand, posed as its graduates? What a vista too, it opens up for adoption by the census takers of our cities which crave greater population? Just count as alive all those who have died before middle age.

As one example of practical work adapted to interest students

in their semi-specialized courses of the first part of the course, the report mentions the problem of compounding a baking powder properly to make it better or cheaper than those on the market, and as another, the design of a cantilever bridge and the determination in what members, if any, high carbon or nickel steel should be substituted for structural steel. These two are certainly far apart as engineering problems. A student who has had the stoichiometry problems incident to an elementary course of chemistry in the high school, should be able to write the reaction for a baking powder mixture and calculate its proportioning, but the latter problem would require such wide knowledge of weights, strength, heat treatment, and cost that the graduate might well envy it.

Quoting from the report; "When the student has completed the semi-specialized work"—requiring two years—"he should be well grounded in the fundamental principles of engineering science and in the *theory and practice* of some one of the major branches of the profession." Is this not a heroic two years' task for a high-school graduate? Then, having been "claimed by the special field for which he is best fitted" instead of "being shoved by routine adminstrative mechanisms down specialized grooves constructed by the faculty" he is now ready to take up electives "of highly technical content." I quote further: "Since the specialized courses are for specialists who have elected them after a long process of vocational selection"—of two years' duration remember—"they should deal with the more abstract and general phases of each subject. For the industrial phase of it, current problems in industrial research, with practice as assistant on some of them are appropriate; for laboratory practice, expert testing and trouble hunting might serve well: on the scientific side, thermodynamics, the ionic theory, differential equations, functions of a complex variable wave motion, spherical harmonics, electromagnetic theory and all types of design, might be given for those whose bent and abilities warrant." From this is it not apparent that students of this ideal curriculum, only two to three years out of the high school, are expected to solve problems which in engineering practice are given to men of large experience only?

Throughout the report there seems to be a remarkable confusion of the province of the trade or vocational school, with that of a

course in engineering. A proper separation of these two divergent purposes and requirements would go far to make the report valuable and usable.

Finally, does the report not fail to measure up to the standard set by itself, in not bridging the gap from theory to practice, from the theoretical discussion of the subject of a curriculum to an actual example for consideration? Would such a curriculum stand the report's acid text of cost, as measured in the student's available time of four years? Is it likely that a longer undergraduate course is generally desirable or likely to be adopted for the average engineer's education?

The student enters our engineering schools at about eighteen years of age. Most have their mode of thought, their habits of initiative and industry, and their life purposes well along toward stability and equilibrium by the time they reach the age of graduation at twenty-two. If they delay entering upon the practice of their profession beyond this, they find it more and more difficult to adapt themselves to the needs of practical commercial conditions. This is particularly true of plant operation and the gaining of practical plant sense and commercial manufacturing facility. It is just here, in the judgment of many practical chemical manufacturers, that the duty of the industries to its recruits should properly begin and where many leaders of these industries prefer it should begin instead of several years later.

While intelligent criticism is desired and is always helpful, it is to be hoped that future critics of the present methods of our engineering education will not assume at the start that these methods are wholly bad and totally inefficient, as is so commonly done.

Results in our chemical industries at least do not warrant such an assumption. I venture to assert that in no other country in the world does there exist so well-trained, so efficient, so resourceful and so successful a body of chemical engineers, particularly in its more youthful portion, than the past few years have shown the United States of America to possess and also to say that our technical and engineering educational methods, at least to some considerable degree, should be credited with this situation, desirable both for material prosperity and for military defense.

DISCUSSION

President WESSON: Gentlemen, you have heard Professor Smith's very interesting report which is now open for discussion.

Secretary OLSEN: Mr. Chairman, I do not think we have much time to discuss it, but it seems to me that this is a very important analysis of The Mann Report, and I think it is a very valuable contribution to the literature of Chemical Engineering Education.

One of the things that were brought out is that the college is not supposed to give practical experience and training, but is expected to give the theoretical subjects, and to leave it to the industries to educate their men in a practical way. And I think there has been a demand in the past that the college shall do this practical training. We have had discussions on that line. Professor Richards, Professor Smith, and myself certainly agree that the thing is impracticable to any great extent, and that if you confine the chemical engineering curriculum to mathematics, chemistry, physics and engineering, and you send your men out with those fundamentals well taught, it seems to me that you can trust the industries to give them the practical education that they need. And there is where The Mann Report falls down most lamentably.

REPORT OF COMMITTEE ON CHEMICAL ENGINEERING EDUCATION

JUNE 8, 1920

Read at the Montreal Meeting, June 28, 1920.

We beg to submit herewith a report of progress. At the suggestion of the chairman a very extensive bibliography on "The Education and Training of the Chemist and Chemical Engineer" was prepared by C. J. West of the Information Department of Arthur D. Little, Incorporated. It is expected that this will prove of much service to the Committee, and it will be included as an appendix to our final report.

We have been in correspondence with 128 colleges, technical schools, and universities concerning their schedules for courses in chemical engineering. A considerable proportion of these institutions are found to maintain no such course. We have, however, carefully analyzed, compared, and tabulated the schedules from 53 institutions, and there will doubtless be additions to this number as other catalogues are available. A number of anomalies and some surprises are found in many of the scheduled courses, and the Committee hopes to include some discussion of these in its final report.

Meantime, your Committee would refer members of the Institute to Bulletin No. 58 of 1919 of the Bureau of Education, Department of the Interior, entitled "Commercial Engineering" being a report of a conference on Business Training for Engineers and Engineering Training for Students of Business. It is believed that every member of the Institute will find material of interest and food for thought in this report and bulletin, and in this connection I venture to quote the three opening paragraphs from the contribution of Mr. John Hays Hammond:

> "This is an era of expansion, and conformably with the change in commercial conditions the function of the engineer has also expanded. From his capacity of an engineer, limited to the determination of technical questions, the engineer of to-

day has come to assume an economic importance in those branches of industry dependent upon engineering skill for their development. He is, indeed, an engineer of limited usefulness who does not go further professionally than to submit a purely technical report on subjects presented for his consideration.

"While he has the same responsibilities as formerly in the solution of the technical problems involved, the engineer is further expected to supplement his report with advice on the financial and commercial aspects of these problems, for the great majority of problems presented to the engineer ultimately involve the determination of the pecuniary relations of the propositions under consideration.

"Moreover, when an engineer recommends the investment of capital in an enterprise he incurs a certain normal responsibility for its efficient management, inasmuch as his professional reputation depends upon the realization of his predictions as to the outcome of the investment. For this reason he passes from the rôle of an expert to that of a consulting engineer, bound to supervise both the technical and the business management of the property financed by his clients."

Your Committee feels that it may with propriety call attention to the fact that whereas the American Institute of Mining Engineers, the American Institute of Electrical Engineers, the American Society of Civil Engineers, and the American Society of Mechanical Engineers were invited to be represented on the Committee on Commercial Engineering appointed by the Commissioner of Education, the American Institute of Chemical Engineers was not included, and it would seem to your Committee desirable that representation be accorded the Institute at any further conferences.

Respectfully submitted,

A. D. Little, Chairman,
Herbert H. Dow,
Joseph H. James,
Albert W. Smith,
Theodore B. Wagner,
James R. Withrow,

Committee on Chemical Engineering Education.

SOME SUGGESTIONS AS TO HOW THE INDUSTRIES CAN HELP THE COLLEGES IN INDUSTRIAL EDUCATION

By A. W. SMITH

Read at the Montreal Meeting, June 29, 1920

During the past five years of strenuous industrial expansion, the dearth of competent technical directors of this growth and their resultant high remuneration has attracted many of the teaching force away from the Colleges and Technical Schools. It has also resulted in diverting the normal supply of recruits from this teaching service to such an extent that the Colleges have sent out a note of warning to the industries.

The cure for this situation has been of late one of the chief topics of discussion, not only among those responsible for the maintenance of a high quality of instruction but equally among the directors of the industries as well. Mediocre or poor instruction for the recruits to the industries would not be long in showing itself in lessened production and growth and particularly in the slowing of the recent rapid advance in improvement and new development. Of all the industries, the directors of Chemical plants have perhaps been most alert to the situation, possibly because hardest hit. This alertness is evidenced by scholarships, fellowships and other helps to chemical students financed by several of the large Chemical Corporations, by the retention in an advisory capacity of College and Technical School professors and instructors by the research departments of Chemical Companies, particularly for summer vacation time service; and especially by a systematic study by groups of the Chemical manufacturers of how they may best help the Colleges in the present crisis.

A well-written and maturely considered paper on the subject of how the Chemical Industries may best help the Universities and Technical Schools was read at the recent meeting of the American Chemical Society, at St. Louis, by Dr. William J. Hale, who has had

the advantage of experience both with the Chemical Department of the University as well as connection with Chemical plant development and operation. I wish to present here a brief outline of his conclusions, a statement of his proposed plan and what seems to me to be a needed addition. His conclusions are as follows:

1. Only those thoroughly grounded in the fundamentals of their science can expect to gain prominence.

2. For the ordinary college or technical school graduate a research problem is recommended, preferably in pure science and under competent guidance, to occupy at least a year previous to other employment. To encourage graduates to enter such research, the establishment of paid fellowships is desirable and the graduate school offers the best opportunity for such broad research training. Our present greatest need is for the selection and development of men of outstanding ability in science, particularly to carry on this work.

I think most of us will agree with these two conclusions, if applied only to those who are to enter industrial development and research work. For those who are to build and operate Chemical plants, probably most would prefer to have this time spent in gaining plant experience and sense.

3. Industrial research may be carried on at University laboratories by the faculty or by especially endowed researchers, provided only that a professor with broad plant experience is available for its supervision. Such are extremely rare. Subjects vital to the particular industry's growth must have their investigators closely connected with the plant itself. Large chemical industries have now come into a full realization of the importance of constant research as essential to vigorous growth and their laboratories lack no needed equipment or tool, no matter how expensive. Even the *Science* of Chemistry in the University is behind its advancement in the industries. For these reasons there is little possibility of direct advance in industrial chemical enterprise through industrial research undertaken in a University laboratory.

4. The University often does not attract, but stifles the ambition and ultimately destroys the progress of gifted young men with a desire for research, by small pecuniary recompense, but more particularly by converting them into teaching drudges, clerks or janitors. Even the professors often evolve completely into purchasing agents, disciplinarians, clerks on Committees of Attendance, and supervisors of janitor service.

5. Chemical Science as a whole will be advanced most, and exceptional young men be encouraged best, by the assistance of pure research in the University and College and the publication of its results, and this will result eventually in the greatest profit to the industries as a whole.

Dr. Hale's plans for improvement are all connected with the last conclusion, and are all devices to encourage research in pure science. They are as follows:

1. Pay to the publishers of original articles, the results of their own research, something analogous to the royalties on books and magazine articles.

2. Award to the fruitful author of accepted research publications some academic title, such as "Assistant Director of Research." The large funds needed for these payments are to come mostly as industry's contribution to the University's needs.

It is assumed that this monetary as well as honorary recognition and reward for research in pure chemistry will not only attract young men of ability to instructorships and stimulate their productive energy, but will also enlarge the productive possibilities of the research professors to direct this work, and so will stimulate the selection and development of men of outstanding ability in our Chemistry faculties, which has been characterized properly as our greatest present need.

Now for my criticism of the plan: While I agree that great teachers are generally men of research productivity and that such men are usually the greatest incentives to high resolve and effort by the student, such is not always the case. We all know many great teachers whose time has been so filled with the routine work of instruction and of laboratory trivialities that no strength has been left them for research, however much they desire such opportunity and however able they may be to accomplish research results. Now great teachers are more essential to the proper start of our recruits for the chemical industries than all other things combined. To return to Dr. Hale's first conclusion, "Only those thoroughly grounded in the fundamentals of their science can expect to gain prominence." Great researchers never have the time necessary to devote to this thorough grounding of students and just here *great* teachers are essential, whether young or old. So along with the stimulation of research in pure science, to the full utility and importance of which I heartily agree, let us also devise and add some method for the stimulation of the production of great teachers of the ground work of our

science. We all know what small rewards in honor and money some of these men receive compared with what their energy and talents would acquire in most other lines of endeavor. I have in mind particularly one such great teacher, Otis Coe Johnson, who gave so many American chemists just such a thorough grounding in elementary chemistry as we are discussing and who received in his lifetime very small recognition at his own College either in salary or position for his great services to the then younger generations, but whose text book on Qualitative Analysis, as revised by our secretary, is still the greatest book of its kind for instructional purposes. Let the plan be so devised as to attract the ablest of our young men as instructors and to retain them as research professors through the research reward, but let the plan also provide positions in our Colleges that will be at least as attractive for the great teachers; to give to the student at the start that example of fine character and noble living service as well as clear instruction which so many of us can remember as our greatest help from the College. This is the type of man that is becoming almost extinct because of the great injustice which the lack of adequate reward does to him, but more particularly to his wife and family.

Finally for a plan by which the industries can assist in encouraging and conserving such teachers. Let it be planned as an assistance to the fittest, by giving help to those technical schools and Colleges which maintain only the highest standards and give the best results. By their fruits ye shall know them. The industries by a proper census can easily ascertain which of the schools furnish them the best-trained men. Then by an endowment fund so add to the salaries of the best teachers in these that they will constitute positions of reward to be looked up to, and an incentive will be added for many good instructors to cultivate the teacher's art and adopt this as a life's work, without looking forward to declining years of hardship and want. This plan of encouraging the best teachers was exactly the wise plan proposed by Mr. Carnegie with the pension fund which he founded and which by trying to spread too thin his administrators have so speedily wrecked. Proper reward to the fittest is the best way to ensure its survival.

The twofold plan then becomes this: Pay young instructors well for distinguished results in research and add a distinguishing title. Pay exceptional teachers in their maturity exceptionally well, so that their reward may be commensurate with that received in business

and the industries. I will not attempt here to work out the details of just how this may be accomplished, but if confined solely to those institutions producing results of exceptional merit, it would be far from an impossible drain upon the industries. If inaugurated by the Chemical industries it would be speedily followed by the others.

DISCUSSION

Vice-President HOWARD: Professor Smith's paper is open for discussion.

Dr. J. W. RICHARDS: How are we going to find "the natural born teacher?" We need him, and the only way to find him is to take the young man and try him out. Right there is where the University needs to get him on as an assistant or an instructor and give him the chance to show whether he can teach.

You operate that sifting-out process while the young man is working for a small salary, showing his ability to teach if he has any, and during that period the University should encourage him to study for his Master's degree. The Universities have there a favorable opportunity to do two things: to discover the "natural-born" teachers, and at the same time to find the research men and give them the opportunity to work.

My experience is that under such conditions these young men are willing to put in their time for just about enough to live on. Their first enthusiasm for science is still increasing, and they are anxious to show what they can do in both those lines, teaching and research.

Universities should develop to the limit this way of recruiting teachers and developing research men, paying them what it can above a bare living salary. At the same time, if there are any scholarships available from the industries, they will assist.

Dr. BASKERVILLE: May I ask of others who have had experience what kind of compensation these men in teaching should receive? I have about sixteen and take on about eight each year. We now give them $700 for ten months to begin with, and any fees which they may have. I think that is fair. We give annual increases of $100 to $200, depending upon the man. I should like to know what they are paying at other places.

Secretary OLSEN: How much teaching do they do, Dr. Baskerville?

Dr. Baskerville: Four sections, or four mornings or afternoons a week. The rest of their time is presumably devoted to advanced work, either at Columbia or at our place, or elsewhere. But they are required to carry on advanced work for advancement.

Professor Badger: We have at the University of Michigan the same situation to meet, in that we can never find enough young men to handle the teaching work, especially in the larger classes. We have tried exactly the plan which Dr. Richards outlined, of getting likely young fellows and giving them a trying out by allowing them to do part teaching work and part work for advanced degree. To such men we are now paying $500 to $750 and their fees, and those will possibly be $30 to $50 a year. These men are in laboratory work, so that it is a little difficult to state the amount of teaching they do, but they are allowed by the graduate school to do perhaps three-fourths of the work which would be required if they were not teaching.

I am speaking for the chemical engineering department of the university, which is entirely distinct from the chemical department. The chemical department uses many more such men than we do. Such men are expected to do probably five or six hours of teaching or the equivalent number of laboratory work, a week. Where the graduate school expects a full graduate student with no teaching to take not less than twelve credit hours of work, these men are permitted to take ten.

We find it very difficult to get even men with a leaning for teaching to come back at that rate, when they can go out at $150 a month in interesting work. We have had no difficulty in placing our June classes at $135 and up. If a man has any experience at all in the line into which he goes, he gets $150 a month, or more. Hence we find it harder every year to attract into graduate and teaching work the class of men we need.

THE MANUFACTURE OF PEAT FUEL AND ITS UTILIZATION FOR VARIOUS PURPOSES

By B. F. HAANEL

Read at the Montreal Meeting, June 29, 1920

Introductory

Means and ways for utilizing the vast quantities of heat energy lying dormant in the peat areas of the world would in all probability attract but little attention to-day were it not for the fact that people, generally, are beginning to realize that the world's stores of solid and liquid fuels are limited in quantity and that with certain of them exhaustion is within sight.

In no age in the history of the world have all the natural resources been exploited on so stupendous a scale and not since the advent of man on this Earth has his prosperity and very existence been so inseparably linked with certain of them. Yet knowing these facts the very sustenance of his life and welfare is being drawn upon at a most alarming rate and it must be said in a most prodigal manner.

This is an era of phenomenal industrial activity based on the marvelous development of the sciences and future historians will perhaps describe this period in contradistinction to others as the mechanical age. Directly, however, the great achievements of to-day are due to the ability we possess of generating power in almost unlimited quantities, and the length of the life of this most spectacular epoch will be measured by the life of mechanical power.

The immense deposits of the various classes of coals have for so long a time supplied man with a cheap and easily obtainable fuel, particularly suited for metallurgical purposes and the generation of power—that but little or no thought has been given to the utilization of the lower grade fuels which perhaps in but a comparatively short time will have to serve as a substitute for both the high-grade coals and petroleum. Peat the subject of this paper is one of the lower

grade fuels, so far as heating value and difficulty of winning are concerned, perhaps it might be described as the lowest grade fuel.

Origin of Peat

Peat is a combustible substance produced by the slow decomposition of vegetable matter in or in the presence of water. The character and quality of the peat depends on the conditions prevailing during the period of decomposition and on the nature of the vegetation taking part in its formation. The peat forming vegetation comprises practically all the mosses—especially Sphagnum and Hypnum—heath plants, sea and swamp plants such as rushes, sedges and grasses and to limited extent trunks and roots of trees, leaves, etc. According to P. R. Bjorling and F. T. Gissing * the peat formation is accounted for in the following manner:

"During the growth of the plants the interior walls of the cells are gradually coated with substances, which ultimately become so thick as to impede the free transpiration of oxygen and aqueous vapor, the result of which is a lowered vitality and finally death of the cell. At this stage the plant generally begins to decompose, the contents of the cell disappearing first, then the cell wall, and lastly the spiral fibers. These steps are marked by characteristic chemical changes. The retention of oxygen in the compounds at the time of death promotes fermentation, especially of the nitrogenous compounds which yield ammonia, sulphuretted hydrogen and phosphuretted hydrogen. The non-nitrogenous compounds, such as the sugars and starches, are converted into the various acids generally produced by decaying vegetable matter. In the course of time the cells become so distended with the products of decomposition that their walls burst permitting the various gaseous compounds to escape. With this new condition the further chemical changes assume a different character, the unaltered vegetable matter is converted into humic and allied acids and carbonic acid while the soluble compounds pass away in solution, finally the cell is emptied of its contents and deprived of its green color if it originally contained chlorophyll. During the next stage the decomposition of the cell wall takes place. This proceeds more or less rapidly depending on whether or not it is incrusted with slightly soluble lime salts, silicates and resinous matters and also on the strength of the vegetable acid solutions in

* Peat, its use and manufacture.

which it is immersed. As a result of the evolution of oxygen, aqueous vapor and carbon dioxide, the resulting mass contains a large and increased proportion of carbon, a small amount of hydrogen and some oxygen in a combined form, generally as a yellow-brown ulmin; but often this is subsequently converted by oxidation into the light brown humin. At this stage in the process the vegetable matter consists mainly of a mixture of ulmin, humin and spiral fibers. During the final stage, the destruction of the spiral fibers and more resistant tissues is greatly assisted by the combined action of frost and moisture. Frost disintegrates the fibers and the black mould-like substance absorbs so much water that it becomes water-logged and sinks to the bottom of the pool in which it is formed. By the accumulation of an overburden of additional matter resulting from like decomposition, this altered substance is subjected to pressure, slow carbonization and to permeation by bituminous and resinous compounds and after a time is converted into what is commonly known as peat."

In order that the above process may proceed as outlined, free access of air must be excluded, otherwise the residue would be gradually oxidized and only the inorganic components left. In the case of a peat bog, however, the material is immersed in water, free excess of air is consequently excluded and the process outlined above results in the gradual accumulation of peat which increases in carbon content at a rate depending on the rapidity with which humification proceeds. The older the peat formation the greater the degree to which humification has proceeded, depending, of course, on the character of the vegetation forming the different peat layers. The deeper layers of the older peat bogs generally are composed of brown to black, heavy and well-humified peat and the deepest layer a brownish black, dense peat containing very little of still recognizable vegetable remains. This class of peat possesses the highest fuel value.

Physical Properties

Peat as it occurs in the natural state, i.e., in undrained areas, is a mixture of water and partially decomposed and disintegrated vegetable matter of varied origin. The quantity of water associated is generally sufficient to saturate or supersaturate the vegetable matter and constitutes from 87 to over 90% of the weight of the mixture.

Even in a well-drained bog the water content seldom falls below 87% and as long as any water remains in contact with the bottom layers the entire peat mass with the exception of the surface, which is continually exposed to the sun and wind, tends to assume the condition of saturation. The water content it will be plainly perceived, is therefore the most obstinate stumbling block to the successful utilization of this valuable fuel resource.

Peat is an exceedingly variable substance, not only are two bogs, situated comparatively near to one another, likely to differ in the character of the material of which they are composed, but the various layers of any individual bog sometimes possess marked differences. With increase in age and depth of the bog such differences of course become less noticeable and finally disappear. Their variation, however, does not seriously affect the value of a bog for fuel purposes—but they do assume importance when it is desired to utilize the peat content for some special purpose.

As stated above the color of peat ranges from light-yellowish, through various shades of light brown, reddish and dark brown to jet black. All peats look darker when they are saturated with water, but the lighter shades become much darker when the peat is macerated and exposed to the air. This blackening is due to the partial oxidation of the more complex organic compounds to simple ones and the consequent liberation of certain gaseous compounds.

The specific gravity varies greatly with the different types of peat. Figures determined for the absolutely dried peat substance, by various authorities ranges from 0.1 for the very fibrous and poorly decomposed peat to 1.06 for the heavy, compact and thoroughly decomposed black varieties. The peat bogs so far examined in Canada, also exhibit considerable variation as regards the specific gravity and density of the peat substance. But this subject has not yet been thoroughly investigated and consequently reliable figures are not available. The specific gravity of the raw peat substance of the Alfred Bog is in the neighborhood of 1.01.

The contents of inorganic matter which constitute the ash, also varies greatly and depends almost entirely on the conditions prevailing when the different layers of the peat bog were formed. The ash content, though usually low, may in some bogs be so high that the peat is useless for almost any purpose. But the ash found in the normal bog does not present any difficulties when the peat fuel made from it is burned for domestic or industrial purposes.

Chemical Properties and Calorific Value

Peat unlike the true coals has a high oxygen content varying from 30 to 40%, a carbon content ranging from 50 to 60% and a hydrogen content of from 5½ to over 6%. Nitrogen in varying amounts is found in practically all peats—but in certain cases the nitrogen content is unusually high. The nitrogen content of all the peat bogs in Canada so far examined, is over 1%, while in several of them it is 2 or over 2%. In other countries peat bogs are known in which the nitrogen content is even higher than this, and in one bog in the Province of Ontario, Canada, the nitrogen varies from 2.5 to 2.8% —determined of course on the absolutely dry peat.

Nitrogen in peat assumes great importance when the fuel is considered from the standpoint of its value for the generation of a producer gas for the production of power or for the production of peat coke. A typical analysis of Canadian peat is:

Carbon	56.0%
Hydrogen	5.2
Ash	6.0
Oxygen, nitrogen and sulphur by difference	32.8

Phosphorus and sulphur occur to a limited extent in all peat bogs. In Canadian peat bogs these elements vary from 0.026 to 0.087 for the former and from 0.218 to 1% for the latter. The higher phosphorus and sulphur contents, however, are only met with in isolated cases and may be regarded as unusual.

The calorific value of absolutely dry peat varies from 8000 to 9500 B.T.U.'s per pound. These values pertain to Canadian peat bogs. In other countries, notably Ireland, a heating value of over 10,000 B.T.U. per pound is not uncommon.

Since peat fuel in the absolutely dry state is never utilized for domestic or industrial purposes, the values above stated are of little significance. The net calorific value is the only one which need be considered. In order to clearly show the effect which the moisture content of the fuel has upon its calorific value, the following curves have been introduced.* Fig. 1 shows the higher and lower calorific value per pound of peat containing different percentages of moisture and the quantity of heat required to evaporate and superheat the

* Peat Lignite and Coal—by B. F. Haanel.

moisture removed. Fig. 2 shows the pounds of moisture contained in the peat substance per pound of dry peat for varying percentages of moisture; the per cent of dry peat available for power or other purposes in the wet peat, and the percentage of the total moisture

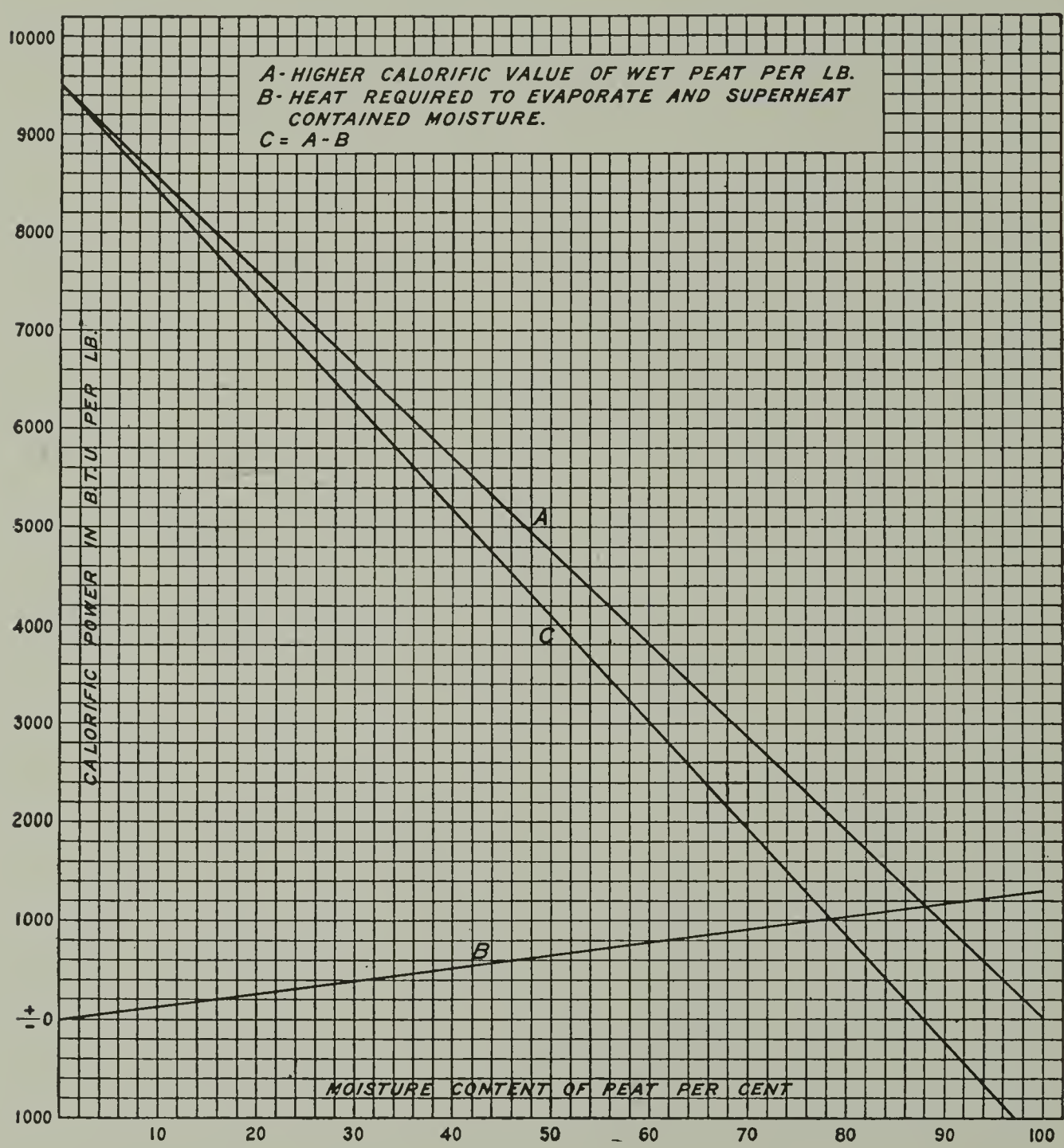

FIG. 1.—Curves Showing the Higher and Lower Calorific Power per Pound of Peat Containing Different Percentages of Moisture and the Quantity of Heat Required to Evaporate and Superheat the Moisture Removed.

contained in the wet peat substance which is removed when the moisture content of the dried peat varies from 0 to 90%. Fig. 3 shows the effect on the calorific value of wet peat by removing different percentages of the total moisture content.

Colloidal Property of Peat

For some time certain investigators who devoted much time to the study of peat held the opinion that the water associated with

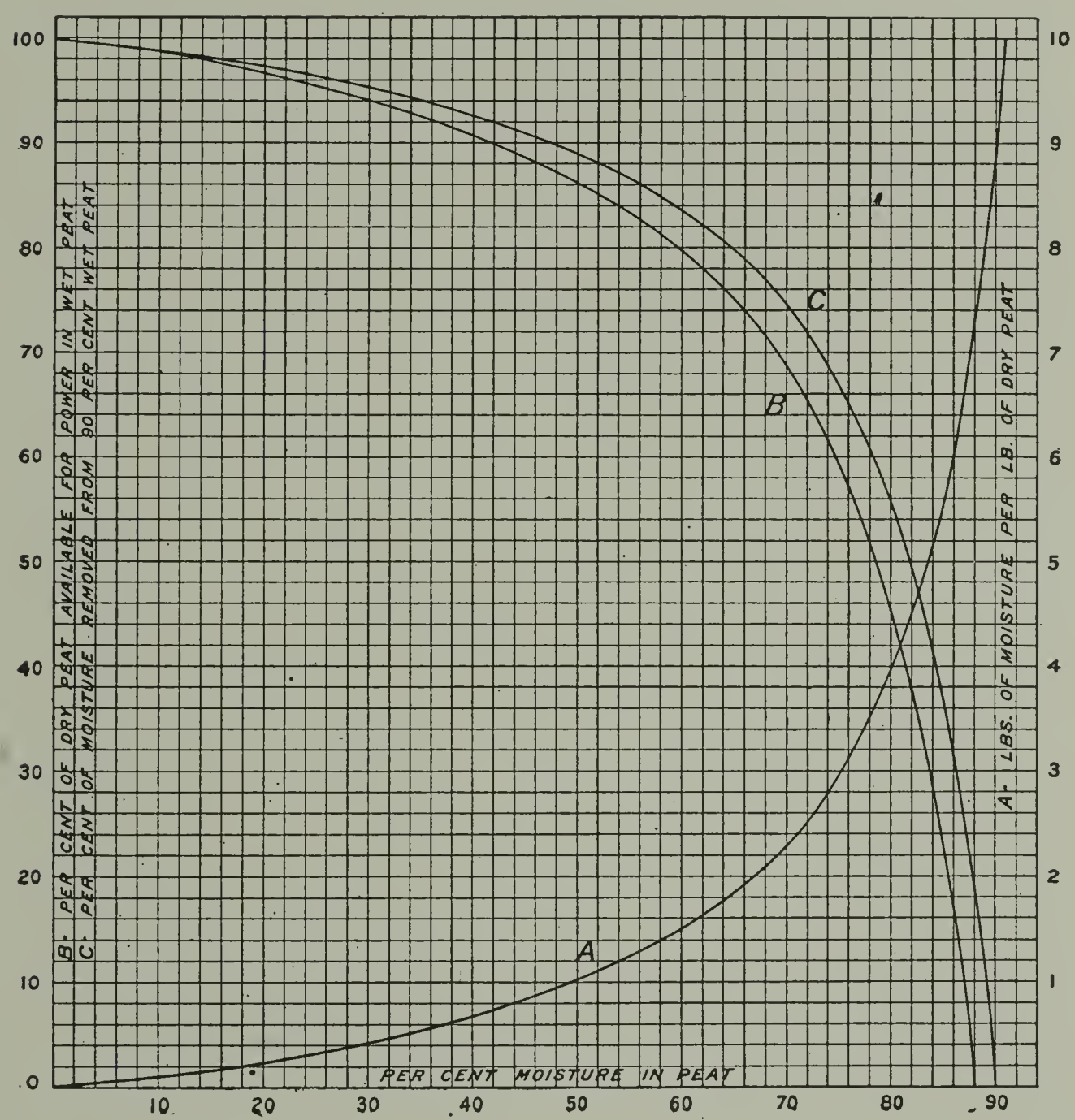

Fig. 2.—Curves Showing Pounds of Moisture per Pound of Dry Peat, for Peat Containing Different Percents of Moisture; Percents of Dry Peat Available for Power of Different Moisture Contents and Percents of Total Moisture Removed from 90 Percent Moisture Peat in Order to Obtain Peat with Different Moisture Contents.

peat was almost entirely held by a complex hydrocarbon termed by them hydrocellulose, which substance possesses the property of absorbing many times its own volume of water and that peat would not part with its water content by pressing until the colloidal prop-

erties of this substance had been destroyed. The name hydrocellulose was given by Ekenberg to a gelatinous hydrocarbon which occurs in all humified peats, to a certain extent, and this hydrocarbon like all gelatines possesses an enormous capacity for absorbing water. This substance, moreover, is a true colloid but the destruction of its colloidal properties or its extraction from the peat mass does not perceptibly affect the capacity of the peat for absorbing water nor render it in such condition that it will part with its moisture by

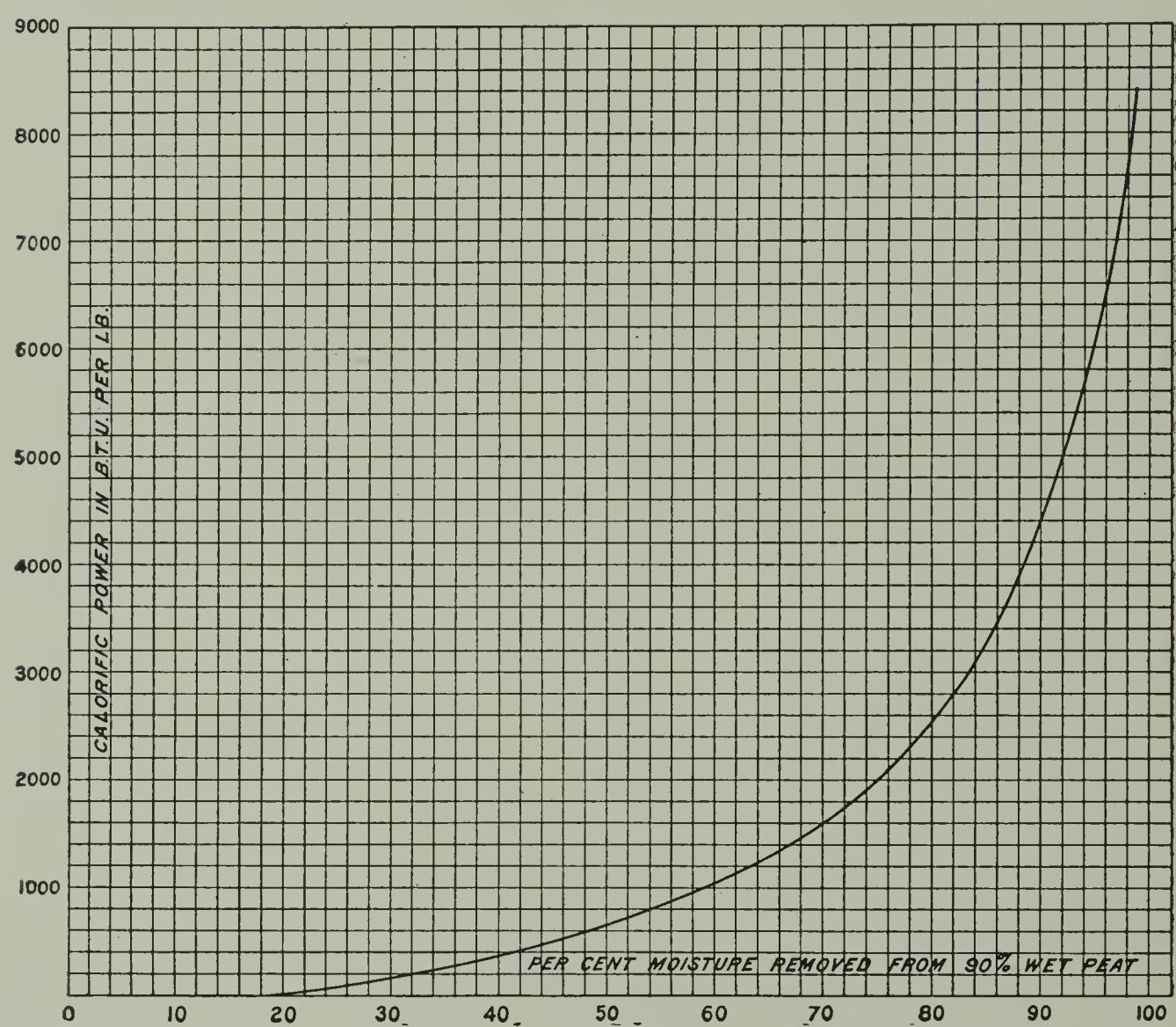

FIG. 3.—Curves Showing the Effect on the Calorific Power of Wet Peat by Removing Different Percentages of the Total Moisture Content.

pressing. The fact is that the better and older humified peats are themselves colloids or at least possess colloidal properties and it is these properties which make it physically impossible to separate the water content, to any great extent, by mechanical means. It is necessary therefore to destroy the colloidal properties of the peat itself if it is desired to attempt to separate the water from the combustible substance by means of pressure. As will be shown later all

attempts to convert the raw peat into some condition which would permit of the water being separated have failed—at least economically.

Manufacture of Peat Fuel

Before discussing the economic methods utilized to-day for converting raw peat into a usable commercial product, it is important to discuss at some length processes which have been tried but which have not proved successful, inasmuch as certain of them not only involve the employment of artificial heat but also pressing by means of either the hydraulic or filter press.

Ekenberg was probably the first investigator who realized that raw peat would have to undergo some change before it could be hoped to separate its water content by pressing and in order to achieve this object he devised a process known as the "Ekenberg Wet Carbonizing Process." By this process the raw peat saturated with water is heated under pressure in a closed retort. A chemical change is effected; the carbon content is increased and some of the hydrogen of the peat combines with the free oxygen, forming water and thereby increasing the water content. No gases are evolved during the period of heating, as in the case of dry distillation, hence none of the combustible components of the fuel are lost.

After the peat has been carbonized in this manner, it is subjected to pressure. While as a result of the carbonizing, the altered peat does submit more readily to pressing, the increased quantity of water which can thus be separated is, in my opinion, not sufficient in amount to enable this process to be conducted commercially. After first carbonizing and then pressing, it is still necessary to employ artificial heat for evaporating the remaining moisture. Efforts, are however, still being made to adapt this process to the manufacture of peat fuel on a commercial scale.

Efforts, which have occasioned the loss of large amounts of money, have also been made to separate the bulk of the water content by artificial drying—first by the direct application of heat as in direct heat dryers; second, by the passing of heated air over and through the mass of wet peat to be dried and third, by blowing large quantities of air at atmospheric temperatures (60° F. and over) over and through wet peat. This last method could be employed only in warm weather. But all of these methods fail when attempts are made to remove the bulk of the water content in this manner, since

there are not sufficient heat units in the combustible substance of 1 pound of raw peat containing 90% water to evaporate the water alone (assuming a dryer efficiency of 100%). Before drying by the application of artificial heat, by any method whatever, can be attempted the water content of the peat must first be reduced to 50% or below—if it be reduced to 50% then for every ton of wet peat containing 200 pounds combustible substance and 1800 pounds of water 1600 pounds of water must be removed by other means than the employment of artificial heat.

In the manufacture of peat fuel great care must be exercised to reduce to the lowest possible limit the quantity of heat which may be required in the process. The reason for this will be plain when the nature of the raw peat substance is thoroughly understood and the low heating value of the combustible substance is appreciated. If peat fuel is to serve as a substitute for coal the cost of manufacture must be kept sufficiently low to enable it to compete with coal in the open market on a heat unit basis. The ratio of the heating value of anthracite coal and peat, when the latter is sold with a moisture content of 25% is approximately 2 to 1. It is, therefore, clear that the process employed for manufacturing peat fuel for industrial and domestic purposes must not entail the expenditure of large quantities of heat nor excessive handling. And in general, ideas of separating the water content by pressing or of destroying the colloidal nature of the raw peat by the employment of electrolytes must, for the present, be abandoned.

Air-dried-machine Peat

For several centuries peat fuel has been utilized on a limited scale by the peasant class of those European countries possessing peat bogs and even to-day comparatively large quantities are prepared by the farming class for supplying their own requirements for heat. The method then employed, and which is still used, in certain places, is exceedingly primitive and the resulting fuel is of very inferior quality as regards its physical properties. This method consists in cutting peat sods and laying them on the surface of the bog for drying, without any further treatment or manipulation. The resulting fuel is, consequently, exceedingly bulky and, in most cases, friable and can, therefore, stand but little handling.

The discovery that puddling, grinding or mastication very greatly improved the quality of the fuel as regards its density,

resistance to absorbing moisture, when once dry, and to breakage, led to the invention of a process known as the Air-dried-machine Peat Process or as it is sometimes called, "Wet Process." This process had its beginning in a very primitive way but through succeeding years with the introduction of machinery and mechanical power it was gradually improved until it reached the state of perfection it enjoys to-day. The most marked improvements, have, however, been made within the past few years.

The process, as it is employed to-day, depends first of all on the forces of Nature—the sun and the wind—for the removal of the bulk of the moisture. The method employing these forces is called the Wet Process and the product is termed "Machine Peat." This is the process which the Mines Branch, Department of Mines, demonstrated with the Government Peat Plant at Alfred some eight years ago and is also the process which the Peat Committee, appointed by the Federal and Ontario Governments, is employing for the purpose of ascertaining whether or not peat fuel can be manufactured on a commercial scale under the conditions at present obtaining in Canada. The Wet Process consists of the following steps: first, the excavation of the raw peat by hand or specially designed mechanical excavators, second, the transfer of the excavated material to the hopper of a specially designed macerator, third, the transfer of this pulped peat to the portion of the bog prepared for drying purposes and fourth, the cutting of the spread peat, when sufficiently set, transversely and longitudinally into blocks, which, when dried to about 25 to 30% moisture have the dimensions of the ordinary building brick.

The macerator which performs perhaps the most important function of the entire process consists of a cylindrical shell, inside of which is a set of spiral rotating knives and a set of knives fixed to the inside of the cylinder. The material fed to the hopper is forced by the spiral knives through and against the fixed knives, the fibers, roots and pieces of wood which are often found throughout the bog are cut, torn or ground into small fragments and the peat composing the different layers of the bog and the gelatinous hydrocarbon previously referred to are thoroughly mixed producing a homogenous mass. The degree to which pulping is carried is determined by regulating the opening of the spout through which the pulped material has to pass.

During the drying stage the gelatinous content of the peat performs a very important function, it serves to bind the particles of

peat together and prevents the peat blocks from reabsorbing moisture when the drying period is interrupted by wet weather. This property which the peat block now possesses is due to the fact that this colloidal substance forms a skin covering the exterior of the block and that this skin always assumes a state of complete saturation until the peat block is thoroughly dry. Hence, it acts as a vehicle for conveying the moisture from the inside of the peat block to the atmosphere. Thus, the moisture evaporated from the outside of the block by the sun's heat is immediately balanced by moisture drawn from within and a state of equilibrium is therefore always maintained until the drying is complete. During rainy weather the reverse takes place; the rain brings the skin to its maximum saturation thus preventing moisture from reaching the interior of the block. As a result of the uniform distribution of the gelatinous material throughout the peat block, contraction takes place as the drying proceeds and the blocks become denser and more resistant to breakage. This characteristic is notably lacking when the peat is manufactured without maceration. When the peat blocks have partially dried on one side they are turned to hasten the drying on the under side. It was formerly considered necessary to pile the peat blocks in small cubes before drying was complete but as a result of our investigations we have found that this step can be dispensed with. The harvesting or gathering of the dried peat blocks from the field must be performed to a very large extent by hand labor with the assistance of power-driven conveying machinery. The above constitutes the various operations which must be performed in the manufacture of air-dried machine peat and all processes for manufacturing peat fuel on an economic basis, to-day, must closely follow the various steps outlined. Up to the beginning of the war a very large quantity of peat was produced in the peat using countries of Europe, notably Russia, Sweden, Denmark and Holland by treating hand-dug peat in the above manner and the plant originally installed near Ottawa by the Mines Branch of the Department of Mines some years ago for purposes of demonstration was similar to those which were employed in Europe at that time. Under the conditions obtaining some seven or eight years ago it was demonstrated that peat fuel could be manufactured at a cost which would permit it to compete with coal, but since that time the cost of labor and of materials have increased to such an extent that so far as Canada, at least, is concerned the old-hand method of excavating the raw peat could not be employed.

In order to manufacture peat fuel on a commercial scale to-day it is necessary first of all to construct machines which will enable the greatest possible capacity per hour to be obtained with the employment of the smallest possible number of men.

With a view to ascertaining whether or not machines could be constructed which would perform these operations at a sufficiently low cost to enable the manufactured peat fuel to compete with coal for various purposes the Peat Committee, above mentioned, was appointed. After thoroughly considering the problems to be solved this Committee decided to construct two types of peat machine, one

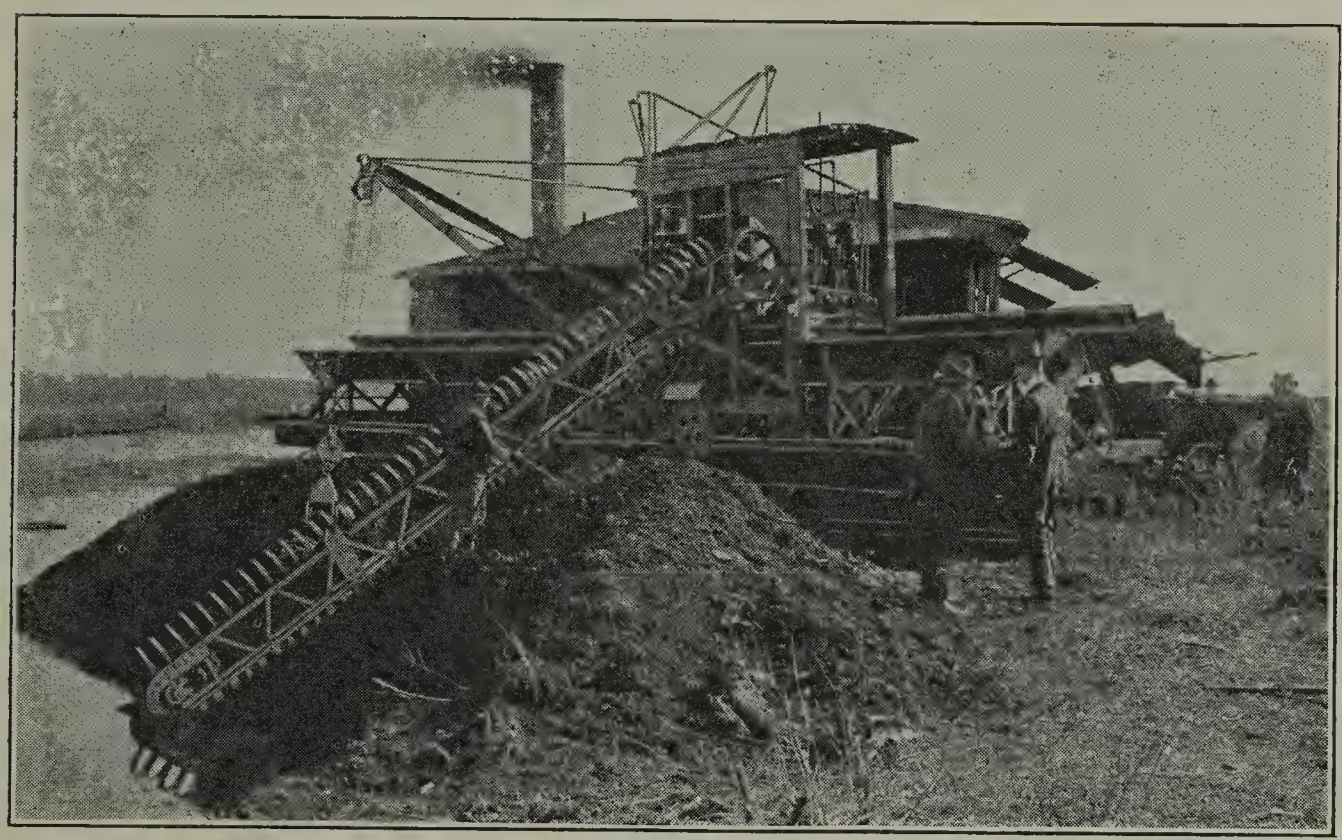

Fig. 4.—View of Anrep Plant Employed at Alfred, Ont.

according to the Anrep system, and the other according to the Moore system. Figs. 4 and 5 show the two machines at work on the bog. The machine designed according to the Anrep system is equipped with a mechanical excavator, which moves to and fro on a fixed track carried by the main platform of the machine. This track is placed at an angle of 45° to the direction of travel of the excavator platform. This enables all standing walls to be left on a slope, which is a highly desirable feature where a heavy machine must be supported close to the excavation. In this manner a prism is excavated of about the following dimensions, 30 feet by the depth of the bog and by the distance of travel of the whole machine. The peat exca-

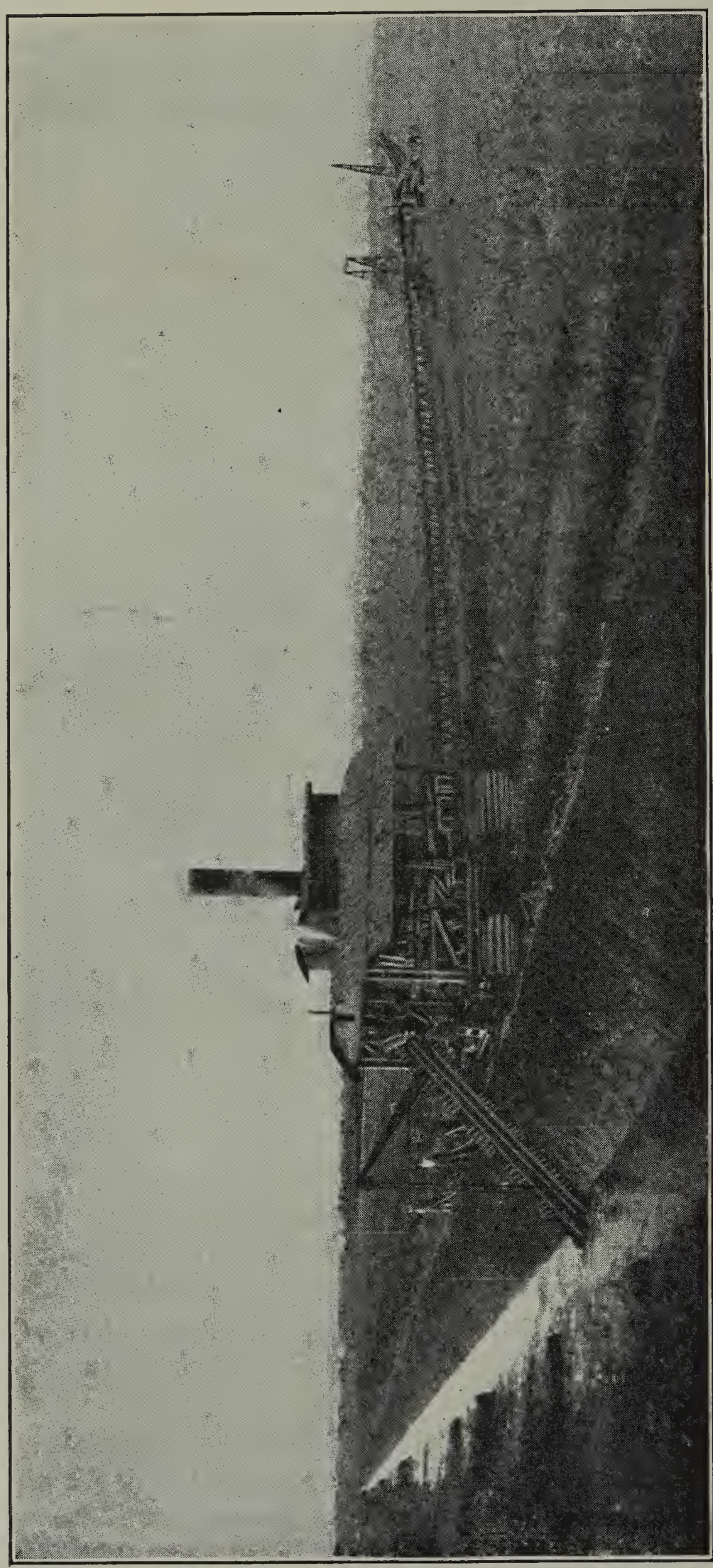

FIG. 5.—View of Peat Machine Designed According to the Moore System.

vated is automatically conveyed to the macerator and from this is discharged into cars which travel around a track system shown in Fig. 6 operated by cable traction from the main machine. These

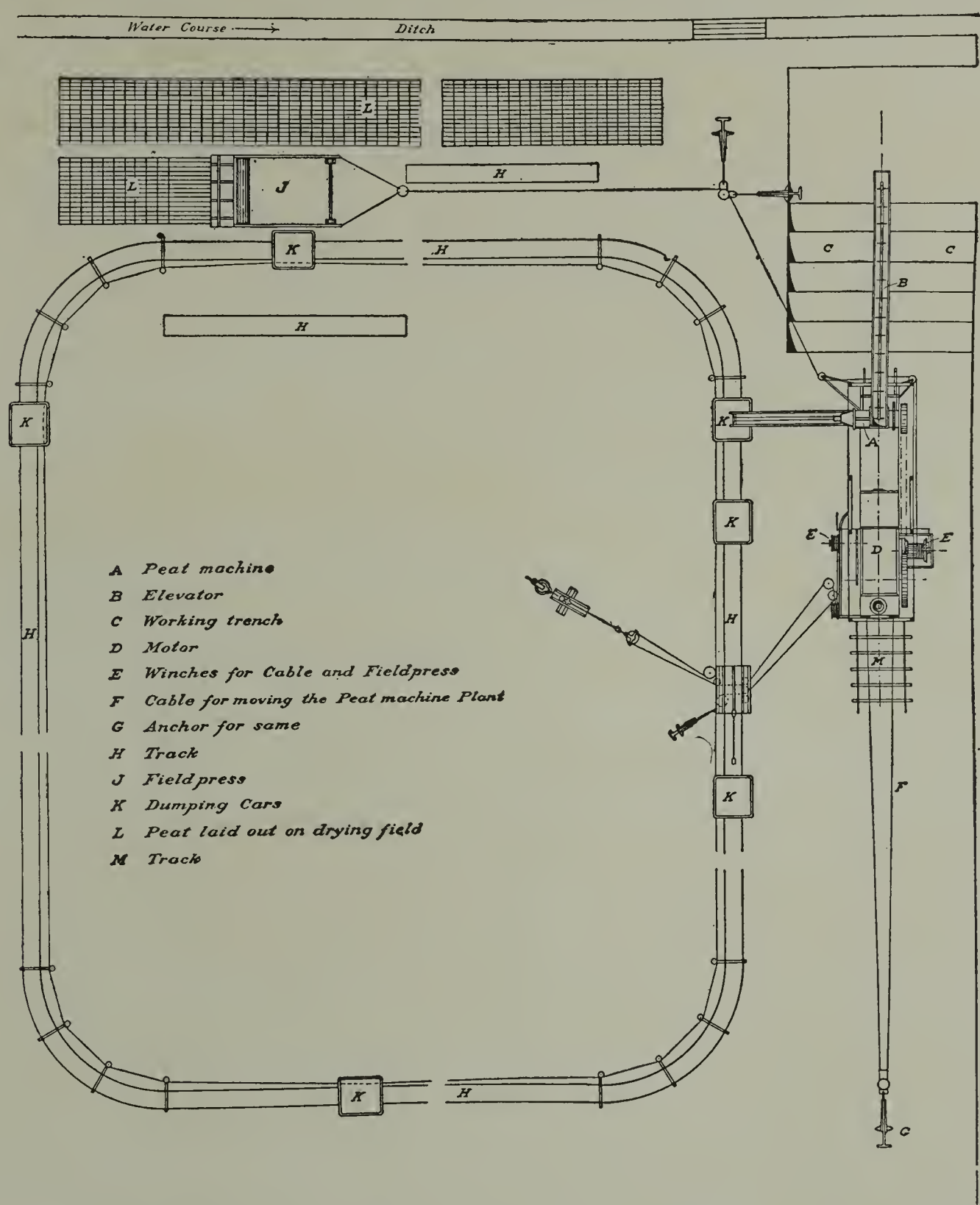

FIG. 6.—Anrep Svedala Peat Plant with Cable Transportation on Round Track and Field Press.

tracks extend to the full width of the drying field, about 800 feet, and the cars discharge into the hopper of a spreader which is operated by a gasoline motor. This spreader lays the peat out in rows 800

feet long. The completion of a row of spread peat necessitates the movement of that portion of the track lying adjacent to it, thus, during the day the track must be shifted six or seven times depending of course on the number of rows laid, and the entire rectangle of track must be shifted every three or four days. In order to overcome the necessity of employing a track system of this description and the consequent expense of moving it after the completion of every row, Moore designed a machine equipped with an excavator which cuts parallel to the direction of travel of the machine. This excavator cuts to only a shallow depth, hence the forward movement of the entire machine is much greater than that of the type described above. The main feature, however, of Moore's machine is the employment of a light bridge work 160 feet long attached at right angles to the main platform of the machine and which moves as an integral part of it. The platform and bridgework are supported and propelled by three parallel caterpillar elements, the driving mechanism being arranged so that all three move forward with exactly the same speed. Provision is made, however, to vary their speed to permit the machine being steered in its course when the working face is not a straight line. This bridge carries a belt conveyor and is also provided with a spreading device and harvesting device which can be attached to it where desired. At the outboard end of the bridge a light elevator is attached which receives the dry peat traveling on the belt and deposits it in a store pile or in the small tram cars employed for harvesting. The caterpillars permit the machines to move over the field under their own power thus obviating the necessity of laying track as had to be done with the original Anrep machine. The peat excavated by the Moore machine is fed into the same type of macerator as is employed on the Anrep machine and is automatically discharged from the macerator into a hopper which, in turn, empties on to the belt conveyor. By means of a suitable sweeping device the belt conveyor is made to discharge at any desired point. It will be seen from the illustration that the peat is laid out parallel to the direction of travel of the peat machine and lays a row of peat equal in length to the working face on which the excavator operates. In the case of this machine the working face as 8000 feet long, hence the row of peat is 8000 feet long by about 12 feet wide. When one row is completed the spreader is moved forward 12 feet and placed on the opposite side of the bridge for spreading the peat in the second row. The machine being symmetrical works equally well

in either direction. This device for transporting the pulped material to the spreader, which is now equipped with an automatic device for cutting the spread peat, longitudinally and transversely into suitable blocks, enables a very marked saving to be made in the number of men it is necessary to employ. In the case of the Anrep machine the spreading system requires nine men as compared with only one man for tending the spreading of the same quantity of material with the Moore system.

The power plant of each machine consists of a water tube boiler of 80-H.P. capacity designed for burning peat fuel and a number of vertical double cylinder steam engines for supplying the power for moving the caterpillars driving the excavator and macerator. Both of the above plants were designed to produce on an average six tons of finished peat fuel per hour, that is, fuel with 25% moisture content, or during a working day of ten hours 60 tons, but with the improvements which have been made from time to time it appears that this capacity will be exceeded in both plants.

The consumption of fuel in the boilers is approximately 3 tons each for ten hours.

Information concerning the value of these machines for the commercial manufacture of peat fuel cannot be given to the public until the report of the Peat Committee has been issued. The above also relates to costs. But it can be said that the results so far obtained are exceedingly promising.

Drying of Peat

An investigation is also being conducted to determine the rate at which drying takes place during the operating period; and also for the purpose of determining definitely when the operations can be begun and when they will have to be terminated. This investigation is not yet complete. As a general rule, that is considering the average summer season in this latitude, it should be possible to manufacture peat for 100 days, including the days lost when it is too wet to perform the operations on the field. To dry wet peat containing 90% moisture which is the average moisture content of the peat slop being spread at Alfred down to 25% moisture requires in the vicinity of four weeks. This period is of course lengthened or shortened by rainy or exceptionally dry weather. Attempts were made to shorten the drying season and at the same time increase the output of the

machines by completely draining the working trench, this resulted in a decrease in the moisture content of the peat to approximately $87\frac{1}{2}\%$, which is the moisture content of the peat in the bog. The 90% moisture peat, above mentioned is due to the free water which is carried by the buckets of the excavator with the excavated peat. The working trench heretofore always contained two or more feet of water and it is this water which was drained off. A decrease in the moisture from 90% to $87\frac{1}{2}\%$ by this means resulted in an increase in the dry peat substance of 25% so that for every ton of peat spread on the field there was 250 pounds of absolutely dry peat substance whereas with 90% water there was only 200 pounds of dry peat substance. The increase in output and the large decrease in the quantity of water which will have to be removed by air drying when the moisture content of the raw peat is reduced to $87\frac{1}{2}\%$ will be better appreciated by the following illustration. In order to produce 1 ton (2000 pounds) of 25% moisture peat, sufficient raw peat will have to be excavated to supply 1500 pounds of dry peat substance, consequently if the raw peat contains 90% water, the quantity of material which requires to be excavated is $\frac{1500}{200} = 7\frac{1}{2}$ tons—water content in $7\frac{1}{2}$ tons 13,500 pounds. With peat containing $87\frac{1}{2}\%$ water, the raw substance will contain 250 pounds of dry peat substance and 1750 pounds of water, the quantity of raw peat required will in this case be $\frac{1500}{250} = 6$ tons. The quantity of contained water will be $6 \times 1750 =$ 10,550. Therefore, in manufacturing 1 ton of peat fuel containing 25% moisture from raw peat containing $87\frac{1}{2}\%$ water, the decrease in the quantity of water which has to be evaporated is $13{,}500 - 10{,}500 =$ 3000 pounds which amounts to over 22% of the total quantity of water in the peat containing 90% water. In other words a reduction of only $2\frac{1}{2}\%$ in the water content of the raw peat means a decrease in the water which must be removed to obtain one ton of air dried peat with 25% moisture of over 22%. Reducing the moisture content of the bog by complete draining would therefore materially shorten the time required to dry the manufactured material down to 25% moisture and would consequently make possible a larger production during the comparatively short working season, by first, increasing the capacity of machine per hour by 25% and second, by permitting a larger production of peat to be spread on the field by virtue of the shorter drying period required.

Peat made in this manner is a clean fuel to handle, and produces little soot or other deposits when burned in an ordinary stove or fire-

place. The ash is in a very finely divided state free from combustible matter, and can be easily removed. When burned for domestic purposes clinkers are not formed and on account of the ease with which the fuel ignites, often, only a little paper or a few shavings are sufficient to start the fire.

Peat fuel on the other hand is more bulky than coal and is, of course, of lower heating value per pound. The relation between Anthracite Coal and Peat Fuel as regards heating value is approximately 12,500 : 6000 or 2 : 1. This is assuming that the peat having a heating value of 9200 B.T.U.'s per pound when absolutely dry is used with a moisture content of 30%. Allowance is therefore made for the heat required to raise the contained moisture to 212° and evaporate it and also the heat required to superheat the steam when the peat is burned in a boiler or gas producer. For a definite quantity of heat, therefore, it will be necessary to store twice the weight of the coal required in peat fuel. The volume occupied by the peat fuel owing to its low specific gravity will also be much larger than that of coal. One cubic foot of ordinary anthracite coal weighs approximately 56 pounds while 1 cubic foot of machine peat weighs approximately 27 pounds. The volume of peat required to equal coal of the above heating value will therefore be roughly four times that of coal. This is a matter of considerable moment and introduces serious problems when large quantities of fuel must be stored.

If it is desired to manufacture peat fuel on a large scale for transportation over long distances by rail it would seem imperative that an effort be made to reduce the bulk of the fuel by increasing its density. This, of course, can be accomplished by briquetting, but before any attempts can be made to produce peat briquettes economically, the raw peat will first have to undergo the treatment just described. After the water content has been reduced by air drying to some 50% it may be economically possible to further reduce the moisture to say 15% by artificial drying. The peat blocks as they are brought in from the field, however, first would have to be ground, the dried fuel could then be briquetted with a suitable binder or used in the form of powder for various purposes.

Action of Frost on Partially Dried Peat

Care must be exercised in the manufacture of Peat Fuel to terminate manufacturing operations in time to permit the manufactured

fuel to be dried to below 50% at least, before severe frost sets in, since, if any of the peat which is manufactured has not had sufficient time to dry down to 50 per cent moisture content before this time it will be frozen and the peat will disintegrate into a fine dust which is useless as a fuel for many purposes. If it is found that peat containing the above moisture content cannot be dried before the cold weather sets in it should be harvested and placed under cover or piled in stacks.

Permissible Moisture Content in Peat

(*a*) *For Domestic Purposes.*—It is customary to reduce the moisture content down to 25 to 30%, but it is even desirable to have a slightly higher moisture content inasmuch as the drier peat burns too quickly and with the ordinary stoves used on this continent it is difficult to control the combustion. Peat fuel containing 30% moisture is also tougher and therefore stands handling better than the drier fuel. In Sweden stoves are especially designed and constructed for burning peat fuel, hence, peat with 25% or less moisture can be used to advantage.

(*b*) *For the Generation of Steam.*—The moisture content of the fuel should not be in excess of 30%, preferably 25% to obtain the best results. With increase of moisture the results due to the heat escaping with the superheated steam becomes considerable.

(*c*) *For Use in the Gas Producer.*—The moisture content should be kept as low as 35%. Fuels with higher moisture content have been used in both the by-product recovery producer of the Mond type and Gas Producers without by-product recovery, but for producer work the best results are obtained with peat having a water content of 35% and under.

(*d*) *For the Manufacure of Peat Powder as Conducted in Sweden.*—It is usual to permit the peat blocks on the field to dry down to 50% moisture. When this degree of dryness is reached the peat is harvested and transported to the factory where it is crushed and ground and then put through a dryer. The driers used for this purpose are specially designed and employ a high temperature, the object being to submit the particles of peat to a sufficiently high temperature to cause the paraffins to sweat out. This forms a coating over the particles and makes them waterproof. For peat powder the moisture content should not exceed 13%.

(*e*) *For the Manufacture of Briquettes.*—It is usual to dry the peat by artificial means down to 15% or lower.

In connection with the moisture content which the peat can have in order to permit it to be efficiently used for the generation of power through the media of the steam boiler and steam engine or a gas producer, extravagant claims have been made that peat with abnormally high moisture contents can be economically used, for example, it has been stated that peat containing between 60 and 70% water can be successfully burned in the by-product recovery producer of the Mond Type. It may be of interest to introduce here the heat balance which was calculated to show the impossibility of generating a power gas in the Mond By-product Recovery Gas Producer with 60% moisture peat fuel. This heat balance is taken from the writer's report "Peat, Lignite and Coal," and was based on the following assumptions:

That all the peat substance is completely gasified.
" " water in the peat is distilled off with the gas undecomposed.
" " air enters the producer saturated at 60° C.
" " steam introduced with the air is decomposed.

Heat Balance

Entering the producer:

1. Potential heat units of wet peat fired = gross calorific power of wet peat.
2. Sensible heat (above 0° C.) viz. air + water at 60° C.
3. Latent heat of steam at 60° C.

Leaving the Producer:

4. Potential heat units in gas generated = gross calorific value of gas.
5. Sensible heat of gases, including the steam, at 200° C. reckoned from 0° C.
6. Latent heat of steam in gases, at 0° C.
7. Radiation losses.

Values Used in Calculation

H = 1, C = 12, N = 14, O = 16.

1 gram mol. occupies 22.4 liters at 0° C. and 760 mm.

Latent heat of steam at t° C. = $101.5 - 0.695t$ calories (Regnault)

Mean specific heats, at constant pressure of

Air,	0°– 60° C.	= 0.237	Regnault.
N_2	0°–200° C.	= 0.244	"
CH_4	0°–200° C.	= 0.593	"
H_2	0°–200° C.	= 3.409	"
CO_2	0°–200° C.	= 0.217	"
CO	0°–200° C.	= 0.245	"
Steam	0°–200° C.	= 0.453	Pier.

Gross Calorific Powers, in Calories per Gram Molecule.

$CO = 68{,}200$
$CH_4 = 213{,}500$
$H_2 = 69{,}000$

Analysis of Peat Burned:

	Dry.	60% H_2O.
Carbon	56.0%	22.40%
Hydrogen	5.2	2.08
Nitrogen	1.9	9.76
Oxygen	30.9	12.36
Ash	6.0	2.40
Water	0.0	60.00

Calorific Power:

Calories per gram	2102.2	
B.T.U. per pound 9460		3784.0

One hundred grams of peat containing 60% H_2O, 86.0 grams of air, and 13.4 grams of H_2O, can give in the producer, 2.40 grams of ash, 60 grams of steam together with 66.82 grams N_2+2.72 grams CH_4+2.89 grams H_2+46.93 grams CO_2+17.64 CO.

The permanent gases are:

2.386 gram mols. N_2+0.170 gram mol. CH_4+1.445 gram mols. H_2+1.067 gram mols. CO_2+0.630 gram mol. CO:

Total 5.698 gram mols. i.e., 127.6 liters.

This gas has the percentage composition:

N_2	41.88%
CH_4	2.98
H_2	25.36
CO_2	18.72
CO	11.06

Calorific power in B.T.U. per cubic foot moist at 60° F. and 30″ Hg.

Gross	147
Net	131

The air in order to carry with it the above proportion of steam must have been saturated at a temperature of about 60° C.

Heat Balance

(1) =	210,220 calories,	(4) =	178,950 calories,
(2) =	2,027 "	(5) =	13,890 "
(3) =	7,570 "	(6) =	36,390 "
		(7) =	9,410 "
Total	219,820	Total	219,820

It will be observed from the above calculation that under the most ideal conditions—which do not and cannot obtain in actual practice—the quantity of heat generated by the burning of peat containing 60% moisture in a producer, is not sufficient to effect the various reactions and provide for losses. It is more within the realm of probability that complete combustion would have to take place in order to permit the production of the necessary quantity of heat.

Briquetting of Peat Fuel

As stated above, when it is desired to transport peat fuel any considerable distance by rail or for that matter by water, and when the question of storing a large quantity of this fuel becomes an important factor, it will be necessary to consider ways and means of reducing its volume so that the heat units per cubic foot will be increased sufficiently to enable it to compete with coal on a more equal basis. This reduction in volume can only be realized by briquetting, but briquetting involves, first, the evaporation of the moisture content of the peat from the moisture content of the air dried peat to 15%, which is the maximum permissible moisture content that peat fuel should have for briquetting purposes. It has been previously pointed out that in order to obtain a large production of air dried machine peat it might be necessary to attempt to dry on the field to only 50%. In this case the quantity of 50% moisture peat which would be required

for the manufacture of 1 ton (2000 pounds) of briquettes containing 15% moisture would be:

2000 pounds 15% moisture peat contains:

Absolutely dry peat	1700 pounds
Water	300 "

2000 pounds 50% moisture peat contains:

Absolutely dry peat	1000 pounds
Water	1000 "

Therefore, 1.7 tons of 50% moisture peat will be required to produce 2000 pounds of 15% moisture peat. The water which requires to be removed to reduce 1.7 tons of 50% moisture peat down to 15% will be $1700-300=1400$ pounds and this would involve the expenditure of $1400\times1120\times\frac{100}{70}=2{,}240{,}000$ B.T.U.'s (assuming that the heat required to raise 1 pound of water from 60° to 212° F. and evaporate it is 1120 B.T.U.'s, and that the dryer efficiency is 70%). If the heat for this evaporation is to be furnished by burning 50% moisture peat fuel, then the quantity of fuel which must be burned is as follows: Assuming heating value of absolutely dry peat to be 9200 B.T.U. per pound, 1 pound of peat containing 50% moisture will have a gross heating value of 4600 B.T.U.'s. The heat required to evaporate $\frac{1}{2}$ pound of water will be $\frac{1}{2}\times1120=560$ B.T.U.'s and $4600-560=4040$ B.T.U.'s will then be the effective heating value of the fuel. To furnish the above quantity of heat, namely, 2,240,000 heat units 554 pounds of 50% moisture peat fuel will be required. Therefore the quantity of 50% moisture peat which would be required to produce 1 ton of briquettes containing 15% moisture—exclusive of the fuel required to supply other quantities of heat required in the process, e.g., power, etc.,—is about 2 tons.

Whether this would be economic or not depends, first, on the cost at which 50% moisture peat can be laid down on the field and transported to the plant for briquetting and second, the ability to supply a sufficiently large tonnage to the briquetting plant to enable overhead charges to be reduced to the lowest possible cost per ton.

Peat can be briquetted with the addition of a suitable binder both in the raw state and when carbonized, in each case the reduction in volume is very appreciable, especially in a carbonized briquette and in addition to being waterproof they can stand rough handling and can be burned without disintegrating in the fire. At the termina-

tion of the work of the Peat Committee it is hoped sufficient data will be available to enable a statement to be made concerning the feasibility of briquetting air dried machine or carbonized peat.

Carbonizing of Peat

Many attempts in the past have been made to carbonize peat, notably in Germany and Russia, and, of course, England, in which country a large amount of work has been done and a large amount of money expended in efforts to produce a fuel by wet carbonizing as stated before. In Germany and Russia, however, the attempts which were made to carbonize peat and for which commercial plants were erected, were confined to the manufacture of a metallurgical coke with recovery of certain valuable by-products. The coking plants which showed the greatest promise of commercial success were those designed by Zeigler—but while they were reported to be operating on a commercial basis and with a profit they were prior to the war closed down. At that time when coal was plentiful and could be obtained at very low prices it was difficult if not impossible for a low-grade fuel like peat to compete with it for such purposes as the manufacture of coke, especially since the value of the by-products derived from peat were not at that time appreciated to as great an extent as they are to-day. What was a commercial failure then, however, might to-day be a commercial success.

In the manufacture of peat coke, as conducted in Germany, the following quantities were obtained by carbonizing 516 tons of peat of the following analysis:

Carbon	35.3%
Hydrogen	3.4
Nitrogen	0.7
Sulphur	0.1
Oxygen	28.4
Ash	0.9
Moisture	31.0

Calorific value, about 6161 B.T.U.'s per pound.

163.7	tons of	peat coke
25.8	"	tar
269.0	"	tar water
330.0	"	gases
0.32	ton of	loss.

The 25.8 tons of tar yielded on distillation:

11.6 tons light oils
3.9 " heavy oils
1.8 " paraffin
7.6 " phenol
0.8 ton asphalt

which is equivalent to 4.5% of the weight of peat coke.

The 269 tons of tar water contained yielded on further distillation:

1.8 tons methyl alcohol
0.9 ton ammonia
2.5 tons acetic acid.

The maximum heating value of gas produced was 344 B.T.U.'s per cubic foot, and the temperature at which retorting took place was about 600° C. The peat coke resulting was of a most excellent character eminently suitable for metallurgical purposes, but its cost per ton was said to be so high that it could not compete with the metallurgical coke made from coal. It will be of interest to include here the results obtained in our own laboratories in carbonizing peat.

Results of Slow Heating up to 650° C. Per Cent of Dry Peat Treated

Total yields in per cent of dry peat

Coke yield	41.4
Tar	12.0
Gas	26.8
Water	19.4
Unaccounted for	0.4

Heat units in products in per cent of dry peat.

Coke	54.7
Tar	20.7
Gas	10.8
Loss	13.8

Peat tar oil, character.

Density of heavy oils	1.029
" light "	0.939
" total "	1.005
Calorific value B.T.U.'s per pound	15,150

Distillation yields percentage by weight of tar.

Up to 170° C.	1.7
" 170°–200°	6.4
" 200°–270°	25.9
" 270°–310°	25.2
Residue	32.5
Water	3.3
Loss	5.0

Gas from peat.

CO_2	43.7
C_2H_4	1.2
O_2	1.7
CO	12.4
CH_4	18.0
H_2	17.7
N_2	4.3
Density	0.98
Calorific value, gross	314
" " net	282

Commercial products.

Coke, pounds per ton dry peat	830
Calorific value B.T.U.'s per pound	12,800
Tar, imp. gals. per ton dry	24
Gas, cubic foot per ton dry	6,600
Cal. value of gas B.T.U. gross per cubic foot	314
Ammonium sulphate pounds per ton dry	25

Utilization of Peat for the Generation of Power and Industrial Gas

Peat has been, and so far as the writer's knowledge is concerned, is to-day being successfully utilized for the production of power:

(1) By burning in specially designed boilers for the generation of steam.

(2) By burning in by-product recovery producers of the Mond Type.

(3) In gas producers without by-product recovery.

(4) For burning in locomotives.

The most notable steam power plant utilizing peat exclusively as a fuel is that erected by the Siemens Electric Company on the Wiesmoor in Germany. This steam plant is of most modern design, consisting of specially designed steam generators, Zoelly steam turbines, and elaborate and well worked out conveying machinery for transporting peat from the sheds to the boilers. The fuel is fed to the boilers automatically and it was claimed that very high boiler efficiencies were obtained, namely, in the vicinity of 73.5%. In dry weather a consumption of 2.4 kilograms (5.28 pounds) per kilowatt hour has been obtained; in wet weather, however the fuel consumption is 3 kilograms (6.6 pounds) and upwards per kilowatt hour. The capacity of this power plant was in the neighborhood of 5400 H.P. when the writer visited the plant. It was said that with peat fuel with 30% moisture costing $1.25 delivered to the plant power could be more cheaply produced than with coal costing $3.50 delivered to the plant.

Peat fuel in the form of powder is employed for generating steam on the locomotives of the Swedish State Railways. There by-product recovery gas producer plants of the Mond Type have been erected for utilizing peat fuel for the generation of a power gas. Two of these plants are situated in Italy, one at Orentano and the other at Codigoro. The third plant in Germany was reported some time ago to be closed down.

Peat containing a high percentage of nitrogen is an exceedingly valuable fuel for burning in the by-product recovery producer, inasmuch as the sulphate of ammonia recovered as a by-product would in certain cases pay the entire cost of operating the plant, thus permitting the power gas or power, when generated, to be sold at a very low cost. There are several bogs in Canada and a number in the United States which in the writer's opinion are especially suitable for the installation of such a plant or plants.

Unless peat fuel can be obtained at exceedingly low cost, it cannot be considered, except in isolated cases, as a suitable fuel for the generation of power when burned in a gas producer of the non by-product recovery type.

Peat Resource of Certain Countries

Before concluding this paper the writer would like to make a few remarks concerning the peat resources of certain of the civilized

countries of the world. The United States, exclusive of Alaska, according to C. A. Davis, late peat expert of the United States Bureau of Mines, possesses 139,855 square miles of swamp lands of which it is estimated that 8% or 11,188 square miles would have peat deposits of good quality. Assuming that the average depth of the peat in this area is at least 9 feet and that the average yield will be 200 tons of salable fuel per acre for each foot of depth, the total available fuel in these deposits will reach 12,888,500,000 tons.

Canada has an area estimated at 37,000 square miles covered by peat a large portion of which is suitable for the manufacture of peat fuel. 12,000 square miles of this area is situated in the more inhabited portions of the Dominion and if it is assumed that this 12,000 square miles is all suitable for the manufacture of a fuel and has an average depth of 6 feet there will be sufficient peat to manufacture over 9,000,000,000 tons of 25% moisture peat.

Ireland alone has 3,000,000 acres of peat bogs having an average depth of 26 feet which is capable of producing over 5,000,000,000 tons of peat fuel. The heating value of the Irish peat, absolutely dry, is on an average 10,000 B.T.U.'s per pound. Other parts of Europe also possess enormous areas of peat bogs.

From the above it will be seen that the heat energy lying dormant in the peat areas of the world may in a short time become a very important factor in maintaining our civilization and while in certain countries the necessity for utilizing this source of fuel may not be immediate, efforts should be made to gain all the requisite knowledge and data which it is necessary to have before peat bogs can be exploited, so that when the time does arrive no time need be lost in the development of the bogs.

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